

Search for a Charge-Transfer State in Crystalline Anthracene

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In this paper we examine the calculation of the location of the charge-transfer state in crystalline anthracene. Also reported are the results of spectroscopic experiments designed to find the transition from the ground state to the charge-transfer state. No experimental evidence could be found for this transition, and it is thereby concluded that: (a) The CT state lies above the first exciton state in anthracene. (b) The polarization energy in the CT state is much less than that calculated on the basis of classical considerations. There is a brief discussion of the nature of the polarization in aromatic crystals, especially with respect to Conclusion (b).

I. INTRODUCTION

IT is well known that ionic contributions play an important role in the excited states of molecules having two or more chromophoric groups,^{1,2} and it is an easy step to suppose that charge transfer between molecules might have a similar role in molecular crystals. Indeed, properly symmetrized and delocalized charge-transfer exciton states are readily defined and, since charge-transfer states do not in general represent stationary states of the molecular crystal, these states may mix with the conventional neutral-exciton states. The role of this configuration mixing has been developed in detail and is discussed elsewhere with respect to the properties of the lowest excited states of neon,³ anthracene,⁴ and naphthalene.⁵ Herein we do not go further with general considerations, but instead focus attention on another problem.

If the charge-transfer exciton states were as different in energy from the neutral-exciton states as 1 eV, then the amount of state mixing would be small and the ionic and neutral exciton states would be reasonably good approximations to the stationary excited states of the crystal. In this case, one might hope to detect the charge-transfer exciton states spectroscopically. On the other hand, if the cited energy separation is only of the order of magnitude of 0.1 eV, then the amount of configuration mixing could be large, and transitions to the charge-transfer states might be hidden by the much stronger transitions to the neutral-exciton states. Of course, transitions to pure charge-transfer exciton states are likely to be relatively weak because of the small overlap of a normally filled orbital on one molecule with a normally empty orbital on a neighboring molecule. Despite this observation, we have

¹ J. N. Murrell and K. L. McEwen, *J. Chem. Phys.* **25**, 1143 (1956).

² H. Labhart and G. Wagniere, *Helv. Chim. Acta* **46**, 1314 (1963).

³ S. Webber, S. A. Rice, and J. Jortner, *J. Chem. Phys.* **41**, 2911 (1964).

⁴ S. I. Choi, J. Jortner, S. A. Rice, and R. Silbey, *J. Chem. Phys.* **41**, 3294 (1964).

⁵ R. Silbey, J. Jortner, S. A. Rice, and M. Vala, *J. Chem. Phys.* (to be published).

attempted to find optical excitation to a charge-transfer exciton state in crystalline anthracene. The results of our experiments and the deductions which can be made are described below.

II. LOCATION OF THE CHARGE-TRANSFER STATE

To calculate the position of the charge-transfer level in the crystal we use a semiclassical approach. Although similar in spirit, the work reported in this section is more extensive than earlier calculations.^{4,6}

To proceed, it is assumed that the energy of the charge-transfer state can be obtained from the ionization potential I , the electron affinity of the isolated molecule EA , together with the direct Coulomb energy of the ion pair C and the energy of polarization of the lattice by the ion pair P . Thus,

$$E_{CT} = I - EA + C + P. \quad (1)$$

Of the data required:

(a) Ionization potentials of polynuclear aromatic hydrocarbons have been obtained from the photoionization experiments of Vilesov⁷ and Watanabe.⁸

(b) Values of the electron affinities of aromatic hydrocarbons are unreliable and almost unavailable. For example, the reported electron affinity of anthracene has ranged from nearly zero to about 2 eV.⁹ In recent years more weight has been attached to the lower values of the electron affinity.¹⁰

Consider, as an example, the calculation of E_{CT} for anthracene. The charge densities at each carbon atom were obtained from Hückel coefficients for the highest filled and lowest vacant Hückel orbitals, respectively, of the ion pair. The Coulomb energy is then computed

⁶ L. E. Lyons, *J. Chem. Soc.* **1957**, 5001; L. E. Lyons and J. C. Mackie, *Proc. Chem. Soc.* **1962**, 71.

⁷ F. I. Vilesov, *Dokl. Akad. Nauk SSSR* **136**, 632 (1960).

⁸ K. Watanabe, *J. Chem. Phys.* **26**, 542 (1957).

⁹ L. E. Lyons, *Nature* **166**, 193 (1950); N. S. Hush and J. A. Pople, *Trans. Faraday Soc.* **51**, 600 (1955); F. A. Matsen, *J. Chem. Phys.* **24**, 602 (1956).

¹⁰ J. R. Hoyland, Ph.D. thesis, Pennsylvania State University, 1961.

as the sum of 14×14 atomic interactions. The polarization energy was taken to be the sum of: (i) the work of inducing dipoles in the lattice, (ii) the work of inducing a dipole in each charge due to the presence of the second charge, and (iii) the interaction of the temporary dipoles with each other and with the dipoles induced in the ions. Contribution (i) was obtained by computing the net field from the 14 atoms of both ions at a lattice site. The dipole-interaction energy was then calculated using the known anisotropic polarizability.¹¹ The contributions to the interaction energy of all molecules in 12 shells around the ion pair in the ab plane and eight shells perpendicular to the ab plane were computed using an IBM 7094. Contribution (ii) was computed in a similar fashion, using the additional assumption that the polarizabilities and the anisotropies of the positive and negative ions were the same as those of the neutral molecule. In obtaining the contribution of (iii) to E_{CT} , it was found necessary to include only molecules in the first three shells in the ab plane.

The results of these calculations for crystalline anthracene, naphthalene, and tetracene are displayed in Table I. We comment on these calculations in Sec. V.

III. ESTIMATED OSCILLATOR STRENGTH FOR THE TRANSITION TO THE CHARGE-TRANSFER STATE

A rough estimate of the strength of the transition to the charge-transfer state can be obtained from a calculation of the transition dipole moment. Since this intermolecular transition depends on the charge distribution at large distances from the molecule, we have followed our previous procedure⁴ and used Hückel orbitals based on $2p\pi$ SCF carbon-atom wavefunctions. The transition moment was found to be $\mu = 3.2 \times 10^{-2}$ a.u. If it is assumed that the transition energy is 4 eV, the computed oscillator strength for the transition to the first charge-transfer state in anthracene is

$$f \approx 8 \times 10^{-5}.$$

Suppose that the absorption band has a width of 0.5 eV, which is not an unreasonable value. Then the transition in an anthracene crystal 1 mm thick would be characterized by an optical density of 1–3. Because of the approximate nature of the molecular wavefunctions, this simple calculation overestimates the oscillator strength of the transition. It should also be noted that the total electronic contribution to the oscillator strength represents an upper limit because of the neglect of vibrational overlap (Franck-Condon principle). We believe the value of f cited to be reliable to within one order of magnitude.

¹¹ R. J. W. LeFevre and K. M. S. Sundaram, J. Chem. Soc. 1963, 4442.

We have already mentioned that the charge-transfer exciton states and the neutral-exciton states mix. It is to be expected, then, that the transition to the charge-transfer exciton state may borrow intensity from the transition to the neutral-exciton state. If

$$\Psi = \Psi_{CT} + \sum_i \lambda_i \Psi_i, \quad (2)$$

where λ_i is determined by the off-diagonal matrix element connecting the charge-transfer state and the i th neutral state and by the energy difference between these states,

$$\lambda_i = \langle \Psi_{CT} | H | \Psi_i \rangle / \Delta E_i, \quad (3)$$

then the contribution to the intensity of the transition to the charge-transfer state is $\sum_i \lambda_i^2 f_i$. For typical aromatic crystals, previous work has shown that $\langle \Psi_{CT} | H | \Psi_i \rangle \approx 10^{-2}$ eV. Thus, neutral-exciton states characterized by oscillator strengths $f_i \approx 0.1$ –1 are expected to lead to intensity contributions of the order of magnitude of 10^{-6} – 10^{-4} to the oscillator strength of the transition to the charge-transfer state. This result is not very sensitive to the separation of the neutral and charge-transfer states, a situation analogous to that encountered in the study of contact charge-transfer complexes.¹²

IV. EXPERIMENTAL DETAILS

In view of the calculations presented in the last section, we have undertaken a search for the transition to the charge-transfer state in crystalline anthracene. Under the conditions to be described, a transition characterized by an oscillator strength of 10^{-5} would be detected. Because of the predicted location of the charge-transfer level, the entire range from the near-infrared to the visible-ultraviolet region of the spectrum was studied.

TABLE I. Calculated energies of crystal aromatic charge-transfer bands.

	Anthracene	Naphthalene	Tetracene
I	7.38 ^a	8.12 ^b	6.88 ^a
EA	~ 0.2	~ 0.0	~ 0.6
C	-2.49	-2.64	-2.4
P	-2.10	-2.0	-2.0
E_{CT} (calc.)	2.6	3.5	1.9
P band	3.1	3.9	2.4

^a Reference 7.

^b Reference 8.

¹² L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc. 79, 4839 (1957).

TABLE II. Vibrational assignment of observed bands in the absorption spectrum of a 1.0-cm-thick anthracene crystal between 4400–12 000 cm^{-1} at room temperature.

Frequency (cm^{-1})	Rel. strength	Assignment	Error (cm^{-1}) (exptl. - calc).	Frequency (cm^{-1})	Rel. strength	Assignment	Error (cm^{-1}) (exptl. - calc).
11 412	m	2×2972+5463 10 160+1262	+5 -10	5 380.7	m	3110+1262+1007 3049+1178+1161 3022+2×1178 2972+1400+1007	2 -7 3 2
10 160±20	m	8739+1398		5 360.5	m	3022+1178+1161	0
8 738.9	vs	2×(2972+1400) or 2×(2972+1378)	-5	5 334.7	m	3022+2×1161 2972+2×1178	-9 7
6 152.2	m (sh)	2×3079	-6	5 193.4	m	3022+1161+1007	3
6 095.9	vs	2×3049	-2	5 174.6	m	3022+1400+751	2
6 062 (mean)	vs (sh)	3022+1558+1478	4	4 973.8	m	3110+1478+388 3049+1400+521 3049+1178+751 3022+1558+388	-2 4 -4 6
6 004.4	vvs	3110+2×1448	-2	4 929.6	ms	3022+1161+751	-4
5 950.8	vvs	2×2972	2	4 917.5	ms	3049+1478+388 2972+1558+388	2 0
5 926.1	vvs	3022+2×1448	2	4 860.1	ms (sh)	3079+1400+388	-7
5 778.8	ms	2972+1631+1178 3049+1558+1178 3110+1400+1262	-2 -6 7	4 853.0	ms (sh)	3079+1262+521	-9
5 712.7	m	3079+1478+1161 3049+1400+1262 2972+1478+1262 2972+1558+1178	-5 2 1 5	4 834.3	s	3079+1007+751 3049+1262+521 2972+1478+388	-3 2 -4
5 641.8	m	3079+1400+1161 3079+1558+1007	2 -2	4 804.1	vs	3110+1178+521 3049+1007+751 3022+1262+521 3022+1400+388	-5 -3 -1 -6
5 585.1	m	3022+1400+1161 3022+1558+1007	2 -2	4 738.0	vvs	3110+1631	-3
5 557.1	m	3110+1262+1178 3079+1478+1007 2972+1400+1178	7 -7 7	4 671.6	vvs	3110+1558	4
5 538.7	m	3110+1262+1161 3049+1533+957 3049+1478+1007 3022+2×1262 2972+1558+1007 2972+1400+1161	6 0 5 -7 2 6	4 645.6	vvs (sh)	3022+1631	-7
5 463.0	m	3110+2×1178 3049+1400+1007 3022+1262+1178 2972+1478+1007	-3 7 1 6	4 613.4	vvs	3049+1558	6
5 418.6	m	3079+1178+1161 2972+1262+1178	1 7	4 600.7	vvs	2972+1631	-2
				4 577.5	vvs	3022+1558	-2
				4 552.5	vvs (sh)	3079+1478	-4
				4 501.2	vvs	3022+1478	1
				4 473.1	vvs	3079+1400	-6

A. Infrared Spectrum

Infrared spectra were taken of three different thick single crystals of anthracene. Two of these were supplied by the Harshaw Chemical Company (1 cm and 0.2 cm thick) and a third (0.5 cm thick) was grown by D. Chandler at the University of Chicago. The last-named crystal was prepared from Eastman H-480 synthetic anthracene and zone refined through 40 passes. The spectra were recorded on three different Cary Model 14 spectrophotometers and covered the range from 4000 to 16 000 cm^{-1} . The thick crystals were used to obtain the positions of the weaker transitions, and thin sections (~ 0.5 mm) cleaved from one

thick crystal were used for fixing the positions of strong transitions. Spectra were recorded at room temperature and also at 77°K.

A total of 65 bands was observed in the infrared region, every one of which could be assigned in one or more ways as an *allowed* overtone or combination. The maximum deviation of the fitted spectrum to the observed spectrum is 10 cm^{-1} , and in general the observed bands are within 2–5 cm^{-1} of the calculated positions. Assignments for the stronger bands are shown in Table II. The assignments are based on the fundamental frequencies of Califano¹³ (infrared) and Man-

¹³ S. Califano, J. Chem. Phys. 36, 903 (1962).

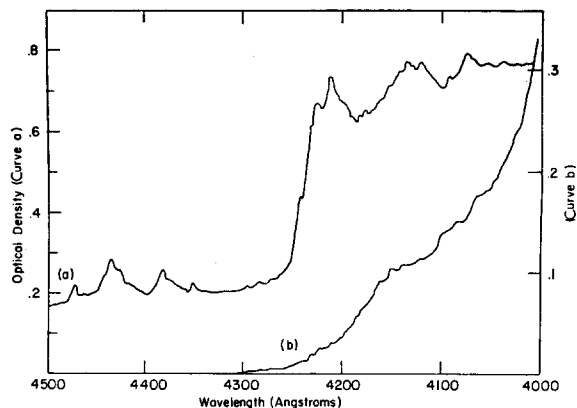


FIG. 1. Ultraviolet spectrum of (a) a thin polycrystalline film of anthraquinone and (b) a thick Harshaw anthracene crystal.

zoni¹⁴ (Raman). A full table of assignments is available on request.

There is nothing in the observed spectrum which suggests the presence of an electronic transition. In addition, infrared spectra were also taken of benzene, naphthalene, biphenyl, and terphenyl. The spectra of all these substances are quite similar to that observed for anthracene.

B. Ultraviolet Spectrum

We have also studied the ultraviolet spectrum of crystalline anthracene at low temperatures from 5500 Å to the free exciton band at 3976 Å. In these studies four crystals were used. Two (0.6 cm) were obtained from the Harshaw Chemical Company, one (0.5 cm) was prepared from Eastman H-480 synthetic anthracene without further purification, and the fourth (0.5 cm) was the crystal grown by D. Chandler and referred to above. The zone-refined crystal was mounted under red safelight illumination to prevent or reduce photo-oxidation to anthraquinone; later the effect of oxygen and ultraviolet light on the spectrum was studied.

The crystals were mounted with Devcon epoxy resin onto a copper rod in contact with a liquid-helium cryostat. The temperature of the crystals, as measured with a calibrated germanium resistor (Texas Instruments, Inc., Model 314) was 14.0°K. The spectrophotometer used was a McPherson Model 225, 1-m vacuum instrument, operated with a tungsten source and an EMI 9514B photomultiplier. Scans were made at 50 Å/min using 15- μ slits.

In addition to anthracene, anthraquinone was studied in the region 4000 to 5500 Å. Sublimed anthraquinone, as obtained from the Eastman Kodak Company, was evaporated from alcohol to form a (nonuniform) layer on a sapphire window. This window was then mounted, using epoxy resin, onto the copper rod of the liquid-helium cryostat. The solution spectrum of anthraqui-

none in toluene was also recorded on a Cary Model 14 spectrophotometer.

Figure 1 shows the low-temperature ultraviolet spectrum of a thick Harshaw anthracene crystal, and a thin polycrystalline film of anthraquinone. In Table III are listed the bands observed, including those seen in the spectrum of the zone-refined crystal. Twenty-one impurity bands were observed in the Harshaw crystals; the crude Eastman H-480 anthracene crystal showed only nine bands; the zone-refined crystal showed seven bands, but with reduced intensity.

Finally, the helium-temperature absorption spectrum of an anthraquinone-doped anthracene crystal was obtained. The anthraquinone concentration was unknown but was much less than 1%. The areas of absorption in the Harshaw crystal, centered around 4220, 4140, and 4020 Å, were all more pronounced in the doped crystal, and discrete peaks were observed at 4019, 4052, 4107, 4139, and 4217 Å.

Previous work on anthracene has shown that the five most probable impurities are phenanthrene, fluorine, carbazole, tetracene, and anthraquinone. Comparing our results with those of Lyons¹⁵ for thin anthracene crystals doped with tetracene (at 4.0°K), we conclude that, since we observed no absorption near 5000 Å where the stronger 0-0 transition of tetracene should be, the bands we have observed cannot be the weaker 0-2 or 0-3 transitions of tetracene. On the other hand, comparison of the anthracene thick-crystal spectrum with the anthraquinone thin-film spectrum shows that every band observed in the anthracene crystal can be accounted for as due to impurity anthraquinone. Lyons also reports that subliming anthracene in air causes bands to appear at 3998 and 4012 Å, and subliming with anthraquinone produces bands at 4013

TABLE III. Observed ultraviolet absorption bands in a thick anthracene crystals and in a thin polycrystalline layer of anthraquinone (wavelength in angstroms).

Anthraquinone	Anthracene	
	Harshaw	Zone refined
3985	3991	3998
4014	4025	4017
4020	4032	4038
4033	4049	4155
4052	4068	4166
4075	4084	4175
4089	4120	4181
4117	4137	
4131	4150	
4140	4162	
4142	4210	
4154	4222	
4157	4231	
4174		
4181		
4212		
4226		
4232		

¹⁴ R. A. Manzoni, Gazz. Chim. Ital. **67**, 790 (1937).

and 4032 Å. The bands we observe at 3998, 4016, and 4038 Å are undoubtedly these same impurity bands. The four remaining bands (4155, 4166, 4175, and 4181 Å) were not reported in the earlier thin-crystal work.¹⁵ The intensity of this set of bands decreased upon zone refining. Furthermore, after the zone-refined crystal, which had been mounted under red light, was exposed to air and ultraviolet light, the intensity of these absorption bands as well as that of the bands at 3998, 4016, and 4038 Å increased, but not to the level of that in the crude crystal.

From the experimental data cited we are forced to conclude that all of the absorption bands observed in crystalline anthracene were due to traces of anthraquinone. Just as in the case of the studies in the infrared region, we find no evidence for an electronic transition to the charge-transfer state.

V. DISCUSSION AND CONCLUSIONS

The experimental results just discussed are obviously negative; an extensive and careful search shows no indication of any charge-transfer state at energies below the first allowed neutral-exciton state of anthracene in particular and of pure aromatic crystals in general. In view of this result, and incidentally of the fact pointed out by Kearns¹⁶ that there is no indication from fluorescence spectra of an excited singlet below the neutral-singlet exciton level, we must re-examine our theoretical model.

The model is used to obtain two reasonably independent quantities: the energy of the ion-pair state and the optical transition probability to this state. Let us examine both of these quantities, beginning with the transition-probability calculation.

The oscillator strength quoted was calculated with the dipole length operator. Intensities of allowed transitions calculated this way are generally too high, perhaps in this case by a factor of 5. The factor of error can hardly be much larger than that because intensity stealing from the first strong transition will keep f above 10^{-5} . It is unlikely, then, that the negative experimental findings are the result of a small oscillator strength. The observed intensity depends on not just the oscillator strength, but on the distribution of intensity among the vibrational states of the system. The calculation of Secs. II and III was based on the assumption that the system be held rigidly or that the equilibrium configurations of both molecules and unit cells are the same for neutral and ion-pair states. (Some allowance for change was implicitly made in the estimation of the observed intensity through the assumption of a half-volt width for the band.) In actual fact, the ion molecules themselves undoubtedly differ in geometry from the neutral molecules, and

the ion-pair unit cell is probably distorted by electrostriction. The intramolecular distortion affects the distribution of intensity, but not, to a good approximation, the oscillator strength. It is unlikely that the band could be spread over more than about 2 eV, so that the intramolecular distortion effect cannot account for the experimental results. The intermolecular distortion will spread the energy also, making the transition easier from excited vibrational states of the crystal than from the ground state; this is an effect whose magnitude we are not prepared to estimate at present, but which is probably no larger than the intramolecular effect. The intermolecular distortion has the second (contrary) effect of increasing the intermolecular overlap and, thereby, of increasing the oscillator strength. The oscillator strength is quite sensitive to the overlap, so that if electrostriction were a large effect, the transition would be quite intense. We believe, therefore, that distortions do not diminish the intensity enough to make the transition unobservable, at least if it is an isolated transition.

Since weaknesses in the intensity calculation do not seem to account for the experimental results, we return to the energy calculation and to the model on which it is based. The model uses charge distributions based on Hückel orbitals and experimental polarizability tensors. We have tried to include intramolecular quantum effects as much as is possible by using these quantities. Intermolecular interactions, on the other hand, have been calculated from the classical model of a fixed ion pair interacting with a polarizable environment. The ion-pair unit cell in its lowest configuration can actually exist in any of eight singlet states, four of symmetry A_u and four of symmetry B_u , in which the charge is delocalized over the unit cell. If we look beyond the unit cell and ask how this ion pair interacts with its environment, we are led immediately to recognize two extreme situations. The first, on which the present calculation is based, is one in which the electrons of the ion pair are strongly coupled to those of the surrounding neutral molecules. Classically, this extreme case corresponds to a polarizable environment which can follow the motion of its polarizing field perfectly: as the dipole moves, the induced polarization moves in phase with it. At the other extreme, the electrons of the ion-pair unit cell are completely decoupled from the electrons of the surrounding molecules. In this weak coupling limit, the neutral molecules respond only to the average field of the ionic exciton, which average field is obviously much more symmetrical than the instantaneous dipole field, and has a much smaller interaction energy with the environment than the dipole does, perhaps even below 1 eV. For example, the charge-transfer state of an alkali halide crystal is close to the weak coupling limit, so that the polarization energy is determined by the field of a quadrupole instead of a dipole.

¹⁵ L. E. Lyons, *Org. Crystal Symp.*, Ottawa, Canada, October 1962, Abstracts, p. 20.

¹⁶ D. R. Kearns, *J. Chem. Phys.* **41**, 581 (1964).

Now, the weak coupling limit obtains when the A_u and B_u stationary states of the ionic exciton are widely split compared with the polarization energy. Conversely, if the Davydov splitting in the ionic exciton is small compared with the polarization energy, the A and B symmetry properties will belong to the unit cell plus its polarization shell, not just to the unit cell, so that the crystal wavefunction *cannot* be written as a product of a single factor representing the neutral molecules and a symmetrized ionic exciton function. Rather, the properly symmetrized ionic exciton function of the strong coupling limit is a sum of terms, each of which is a product of ion-molecule functions multiplied by polarized neutral-molecule functions.

We are not prepared now to say just where the aromatic crystals should be placed with respect to these two limits, but our inclination, as our model must indicate, is to classify them near the strong coupling limit or perhaps even midway between the two. We say this on two grounds. First, the known Davydov splittings¹⁷ of aromatic crystals are small compared with our calculated polarization energies. In the excited ionic state we might expect them to be comparable at best. Second, we can estimate the natural Bohr period for a charge pair moving with an orbit whose radius is the anthracene nearest-neighbor (center-to-center) distance and with an effective mass adjusted to make the orbit stable. The frequency for the free motion of this system is a factor of 4 smaller than the frequency of the first allowed transition of anthracene, the frequency at which the classical picture of in-phase polarization breaks down completely. On these two grounds, then, we suspect that the aromatic crystals are closer to the strong than to the weak coupling limit.

That the crystals are closer to the strong coupling limit implies only that the classical fixed dipole model is the better first approximation for a computation. It does not imply that the polarization-energy calculated from the classical model will be accurate. Rather, it is reasonable to expect the polarization energy to drop considerably if charge symmetrization is introduced. It is our current feeling that charge symmetrization or charge motion is the principal factor missing from the calculations of the energy of the charge-transfer state, and that its omission is enough to push

¹⁷ D. S. McClure, *Electronic Spectra of Molecules and Ions in Crystals* (Academic Press Inc., New York, 1959).

the calculated energy of the charge-transfer state above that of the first neutral-singlet exciton. As Table I shows, any error of more than half a volt in the polarization energy does just that.

Unfortunately, we can no longer rely on a calculation and experiment of this kind to set an upper limit on the electron affinity of anthracene, because we do not yet know how large the error in the polarization energy may be. If the polarization energy were correct as it stands, then the electron affinity of anthracene would be -0.3 eV or less. We prefer to believe that this quantity is positive, probably small, and that the polarization energy as calculated is at least 0.5 eV too large.

In closing, we wish to comment on some bands recently observed in crystalline benzene and interpreted as transitions to higher charge-transfer (Wannier) states.¹⁸ The first member of the observed series (at $38\,702\text{ cm}^{-1}$) is probably the 0-0 transition of the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ band of benzene. However, the assignment of the remaining transitions is not convincing for the first band is assigned to $n=3$, which is correct for the Rydberg states of the isolated molecule, but not for the crystal states. In view of the anisotropy of crystals of aromatic molecules, it is not at present clear whether or not the energies of the lower charge-transfer states should satisfy a Rydberg relationship. It is emphasized that the spectrum of donor-impurity-doped germanium shows considerable deviation from the simple Rydberg-type formula for the lower excited states.¹⁹ This deviation arises from central-cell corrections and the anisotropy of the effective mass. In view of the results cited herein, extreme care should be used in identifying charge-transfer (Wannier) exciton states in molecular crystals.

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¹⁸ A. Ciaia and P. Pestel, *Compt. Rend.* **257**, 654 (1963).

¹⁹ R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963).