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SPECTRA OF ARYLARSINES—II

SPECTRAL MANIFESTATIONS OF CHARGE TRANSFER CHARACTER

W. R. Cullen and B. R. Green
The Department of Chemistry, The University of British Columbia,
Vancouver 8, B.C., Canada

and

R. M. Hochstrasser
John Harrison Laboratory of Chemistry, The University of Pennsylvania,
Philadelphia 4, Pennsylvania

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Abstract—The results of a Murrell type charge transfer calculation on a typical phenylarsine are presented and discussed in regard to the parameters which might change from one type of phenylarsine to another. It is concluded that this theory is appropriate to phenylarsines although the details remain doubtful because of the sensitivity of the theory towards unknown parameters such as β, and such as the 'prepared state' ionization potentials for arsenic in these molecules.

Experimental measurements of the spectral effects of aromatic ring methyl substitution, and of specifically interacting solvents are presented for five new compounds. The slight influences of these perturbations are discussed and interpreted on the basis of the aforementioned theory. It is re-emphasized that a realistic test of the applicability of a theory of diffuse molecular spectra is its ability to predict small variations under such perturbations.

Certain spectral comparisons are made with other molecules containing aryl groups and heteroatoms with lone pairs.

THE objective of this paper is to show that the spectra of arylarsines can be satisfactorily interpreted in terms of an intramolecular charge transfer model. Since the diffuse spectra of such complex molecules provide a flimsy basis for the appropriateness of a molecular theory, this article also presents data on the slight spectral changes caused by alkyl substituents and by solvent effects. These small variations are discussed on the basis of the charge transfer model.

In Part I(1) the gross spectral features of some triphenylarsine derivatives were examined and the solvent sensitive bands which appeared in the region 2200–2500 Å were explained in terms of absorption to states having partial intramolecular charge transfer character. The effect of replacing one or two of the phenyl groups by —CH_3 or —CF_3 was consistent with this interpretation. The present article is divided into three parts: the first concerns the theory as applied to phenylarsines; the second reports some spectra of new ring-substituted arsines; and the third is a qualitative discussion of such spectra and solvent effects in terms of the theoretical model.

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(1) W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spec.* 5, 118 (1960).

I. FORMAL DESCRIPTION OF THE SPECTRAL BANDS

The two principal types of interaction occurring in molecules of the type AsX_3 (X = aryl) are:

(i) Interactions between the aryl groups.

(ii) Charge transfer interaction between the locally excited (*LE*) states of an aryl group and the states of lone pair electrons on arsenic.

In (i) the off-diagonal elements for the interactions between $\pi\pi^*$ states should each be very small. In benzene the B_{1u} and B_{2u} states are electronically forbidden and their vibronically induced stolen intensity should not contribute much to the interactions between the separated systems. Consequently the energy corrections to the B_{1u} and B_{2u} states should be small. However the intensity corrections need not be negligible especially for the weakest B_{1u} (L_b) band. Qualitative estimates of the interaction energies between the states in the three rings, assuming no overlap of π-electron charge distributions of the different rings, indicates that only the allowed E_{1u} state requires an appreciable energy correction ($\sim$0·1–1 eV) but this has been neglected since it has little effect on the semi-empirical calculation of type (ii) interactions.

The influence of the arsenic lone pair on the *LE* states of benzene can be estimated using the semi-empirical method of MURRELL and LONGUET-HIGGINS.(2) MURRELL(3) has done the analogous calculation for anilines. The least certain aspect of this calculation is the choice of a magnitude for the C–As resonance integral, β. Most of the ensuing discussion refers to the model molecule in Fig. 1.

The energy of the zeroth order *CT* states were obtained from the following relation:

$$E_{CT}^{(k)} = I - A - \sum_{i=1}^{6} q_{ik}\, e^2 r_{oi}^{-1} \tag{1}$$

The choice of ionization potential (I) for an arsenic lone pair electron presents another source of error, since this is affected by the substituent. The relevant ionization potentials that are known are: arsine, 10·6 eV; trimethylarsine, 8·3 eV; dimethylarsine, 9·0 eV; methylarsine, 9·7 eV; $(CF_3)_2AsH$, 10·9 eV.(4) In our calculations we have used a range of values from 10·6 to 9·0 eV. In Equation (1), A is the electron affinity of benzene, for which the value of —0·54 eV was used.(5) The last term of Equation (1) is the Coulomb interaction; q_{ik} is the coefficient of the ith benzene atomic orbital for the kth self consistent field molecular orbital; e is the electronic charge and r_{oi} is the distance between the arsenic atom and the ith carbon atom in the benzene ring. The C–As distance used was 1·99 Å. When the electron jumps from the arsenic atom into the lowest unoccupied benzene orbital which is doubly degenerate two zeroth order CT states result:

$$\begin{aligned} E_{CT}^{(1)} &= I - 4{\cdot}27\ \text{eV} \\ E_{CT}^{(2)} &= I - 3{\cdot}62\ \text{eV} \end{aligned} \tag{2}$$

The former mixes B_{1u} and E_{1u} type benzene states and the latter mixes the B_{2u}, E_{1u} and ground states of benzene. The 3 × 3 and 4 × 4 energy matrices were diagonalized

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(2) J. N. MURRELL and H. C. LONGUET-HIGGINS, *Proc. Phys. Soc.* A **68**, 329 (1955).

(3) J. N. MURRELL, *Proc. Phys. Soc.* A **68**, 969 (1955).

(4) W. R. CULLEN and D. C. FROST, *Canad. J. Chem.* **40**, 390 (1962).

(5) N. S. HUSH and J. A. POPLE, *Trans. Faraday Soc.* **51**, 600 (1955).

to yield wavefunctions and energies for seven states of the composite molecule. The results can be brought into agreement with experimental spectra of $(CH_3)_2As(C_6H_5)$ and $(CF_3)_2As(C_6H_5)$ by choosing $\beta = 2{\cdot}0$ eV and $I = 9{\cdot}5$ eV for the former, and

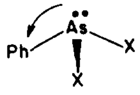


Fig. 1

$\beta = 1{\cdot}5$ and $I = 9{\cdot}98$ eV for the latter molecule. It is possible to force the theory to fit the spectra of all compounds for which we have spectral data.(1) The details of the calculations follow exactly those already described by Murrell.(3) The important result is not the numerical agreement but rather that the *CT–LE* interaction model provides an acceptable description of the spectra. The influence of the unfilled arsenic valence shell (i.e., 3*d*-orbitals) was not examined theoretically.

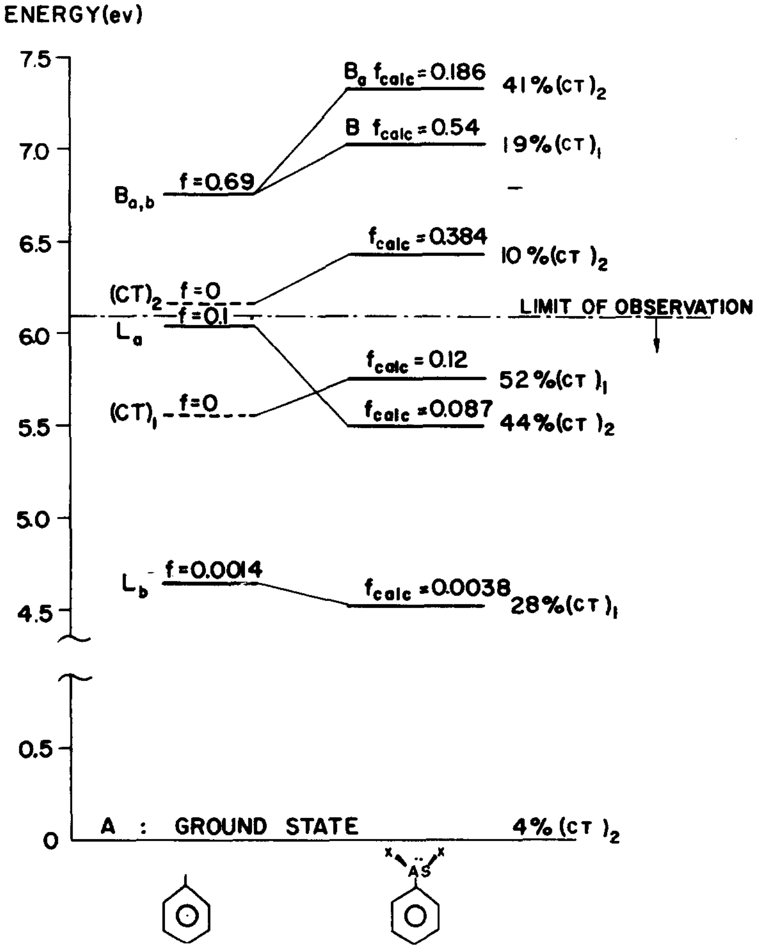


Fig. 2.—The effect of *CT* interaction on the electronic states of toluene.

The energies and intensities of a typical set of states arising from *CT–LE* interaction are shown schematically in Fig. 2. The amount of *CT* character in each state is also noted in the diagram.

The influence of hydrogen bonding solvents on the band positions can be calculated if it is assumed that the principal effect of solvent is to change the ionization potential of the arsenic electrons. The results are shown in Fig. 3, which translates band shift into change of ionization potential. These data refer to $\beta = 1{\cdot}50$ eV. The ratio of the change in ionization potential to the corresponding band energy change is the factor by which our solvent shifts must be multiplied in order to make crude estimates of the solvent stabilization of the lone pair. The data of Fig. 3 show that observed solvent shifts can relate to three or four times this amount of orbital stabilization. Therefore within this framework an observed solvent shift of 300 cm^{-1} to higher energy, relates to about 10^3 cm^{-1} ($\sim$3 kcal/mole) of orbital stabilization.

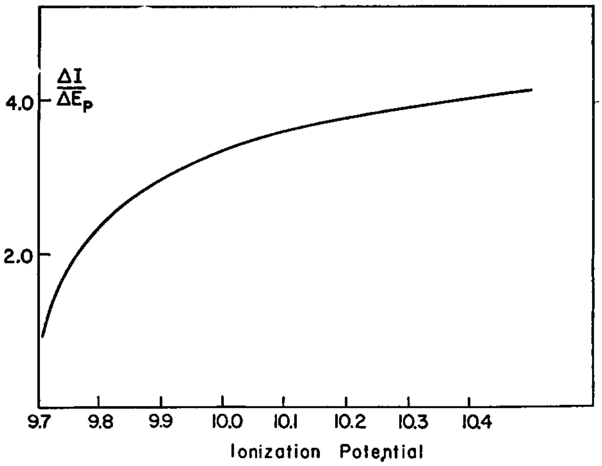


FIG. 3.—The effect of ionization potential of a donor non-bonding electron on the ratio $\Delta I/\Delta E_p$. ΔI is the change in ionization energy required to cause a spectral shift ΔE_p of the L_a band.

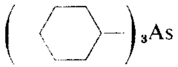
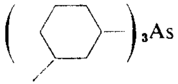
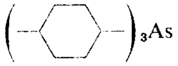
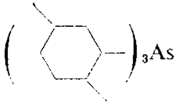
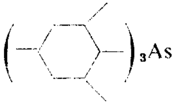
II. THE INFLUENCE OF RING SUBSTITUENTS ON THE SPECTRUM OF TRIPHENYLARSINE

The details of each absorption spectrum are summarized in Table 1. Fig. 4 shows the absorption spectrum of triphenylarsine, tri-*o*-tolyl, and tri-*m*-tolylarsine; and Fig. 5 shows the spectra of tri-*p*-tolyl, tri-*p*-xylyl, trimesitylarsine. Fig. 6 shows the spectra of the corresponding *m* and *p*-trifluoromethyl compounds. A summary of the main features arising from the experimental data of Table 1 now follows.

The intense band in the region 2700Å

Methyl substitution. The maximum extinction coefficient of the short wavelength transition was significantly different from that of the parent molecule (triphenylarsine) only when the rings contained a single methyl group para to the arsenic atom. The energy of maximum absorption decreased through the monosubstituted series in the

TABLE 1.—THE SOLVENT SENSITIVE BAND
THE SPECTRAL FEATURES OF RING-METHYL-SUBSTITUTED TRIPHENYLARSINES

i	Molecule	Absorption maximum in methanol (A)		$\epsilon_{max} \times 10^{-3}$ l. mole^{-1} cm^{-1}		$\Delta\nu$† $1 - i$		$\Delta\nu$‡ solvent	
		R = CH_3	R = CF_3	R = CH_3	R = CF_3	R = CH_3	R = CF_3	R = CH_3	R = CF_3
1		2465*	2465	13·1	13·1	0	0	310	
2		2550		13·4		1,360		120	
3		2490	2465	13·4	11·9	440	30	200	500
4		2480	2525	20·4	14·3	290	990	250	230
5		2565		15·9		1,610		220	
6		2740		16·4		4,120		120	

* Value previously quoted, 2480A (Reference 1), was in error due to faulty calibration of the spectrophotometer.
† Energy of maximum absorption of molecule 1 minus energy of maximum absorption of molecule i.
‡ Energy of maximum absorption in methanol minus that in cyclohexane.

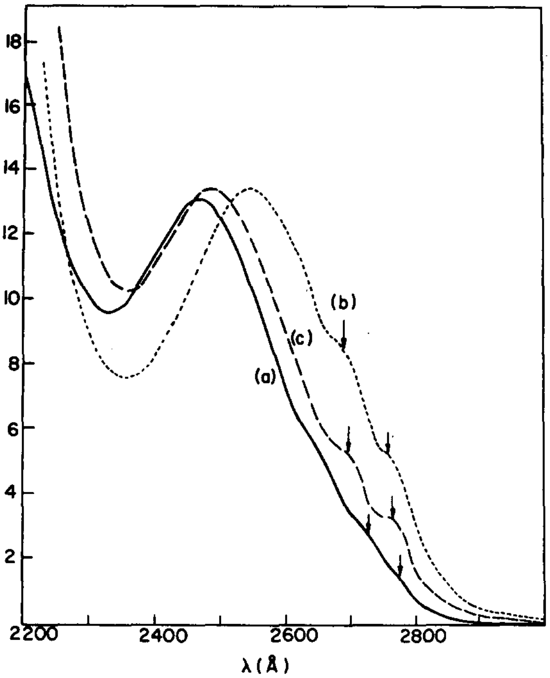


FIG. 4.—Spectra of (a) triphenylarsine, (b) tri-*o*-tolylarsine and (c) tri-*m*-tolylarsine

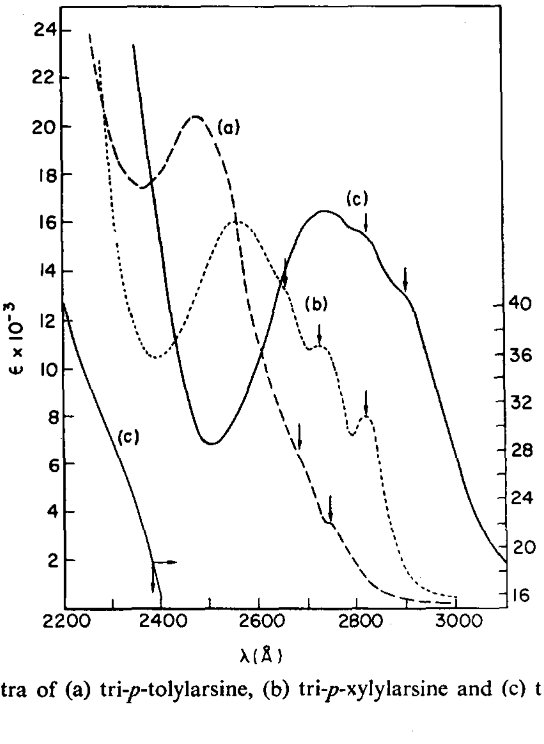


FIG. 5.—Spectra of (a) tri-*p*-tolylarsine, (b) tri-*p*-xylylarsine and (c) trimesitylarsine.

order: $\nu_{\text{para}} > \nu_{\text{meta}} > \nu_{\text{ortho}}$. A further large decrease occurred on going to the dimethyl derivative and a still greater decrease was observed in the case of the trimesitylarsine. Generally the absorption maxima appeared at shorter wavelengths when the solvent was methanol than when it was cyclohexane. The extent of this ***blue shift*** decreased throughout the series para > meta > ortho. The blue shift for every methylated compound was less than that for the parent triphenylarsine.

Trifluoromethyl substitution. Only the *p*- and *m*- derivatives of triphenylarsine were studied since attempts to prepare *o*- compounds were unsuccessful. In this case the effect of *p*-substitution was not to increase the intensity significantly. The energy of maximum absorption increased in the order $\nu_{\text{para}} > \nu_{\text{meta}}$, the reverse of that found in the methyl spectra.

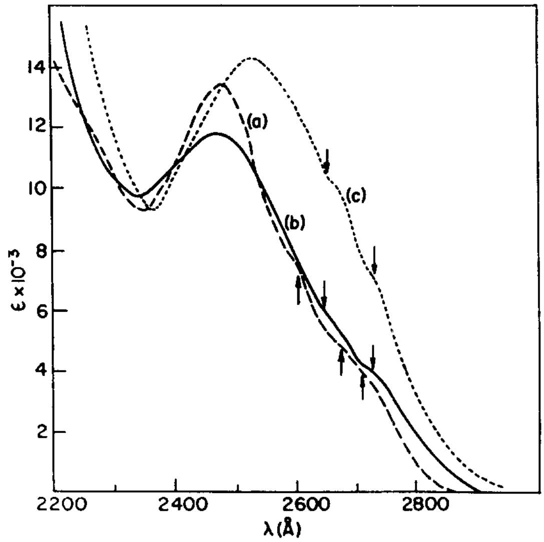


FIG. 6.—Spectra of (a) tri-*m*-trifluoromethylphenylarsine (b) tri-*p*-trifluoromethylphenylarsine.

The benzene ^1L_b band

Methyl substitution. In each of the broad spectra there was some finer structure on the low energy side of the strong absorption peaks referred to above. This band system resembled the ^1L_b band of benzene in intensity, in spectral location, and in the magnitudes of the vibrational intervals. The origin of the absorption (taken to be the energy of the maximum of absorption of the lowest energy vibrational envelope) progressively red-shifted throughout the series triphenyl, tri-*p*-tolyl, tri-*m*-tolyl, tri-*o*-tolylarsine, and the polymethyl derivatives were still further red shifted. For these bands solvent blue shifts were observed, but they were negligibly small (<50 cm^{-1}) compared with those of the strong band, and could have been caused by shifts of the long wavelength tail of the higher energy transition, on which the ^1L_b bands are superimposed at the temperature of these experiments.

The weak bands of this type in the spectrum of any one compound did not shift to the red on methyl substitution to the same extent as the higher energy band. They were therefore assumed to be separate electronic transitions. For example, the 2463 Å band of triphenylarsine was blue shifted by 4,120 cm^{-1} in the tri-mesityl derivative. The weaker bands (L_b) blue shifted by only 2,200 cm^{-1} under the same substitution. These shifts can be compared with those caused by three methyl groups on pure π, π^* bands; the benzene 2050 A band red shifts by 2000 cm^{-1} in mesitylene while the 2500A band (^1L_b) red shifts by 450 cm^{-1}(6) under the same substitution. The present results showed an approximately linear relationship between the energy and the intensity of the ^1L_b band in accordance with theoretical predictions.(7)

In the spectrum of the trimesityl compound there was a third band at 2150 Å. This is seen on Fig. 5 as a slight inflexion on the blue tail of absorption spectrum (c).

Triphenylmethyl substitution. As before, the relative shifts of the strong bands and the weak long wavelength bands under the influence of both solvent and substituent indicated that two separated electronic transitions were involved. The arrows in Fig. 4 indicate the locations of some of the weak L_b bands.

DISCUSSION

The strong solvent sensitive bands are associated with an electron transfer process similar in nature to the charge transfer bands of weak donor-acceptor complexes. Both the donor (the arsenic non-bonding electrons in the non-bonding (L) orbital) and the acceptor (the antibonding π-orbitals of benzene) belong to the same molecule.

The intensity variations

The variations of absorption intensity in methyl substituted aromatic hydrocarbons can in many cases be predicted from simple dipolar considerations.(8) A knowledge of the spectral intensities of a series of systematically substituted benzenes can consequently permit a prediction of the direction of the transition moment dipole for a particular electronic excitation. The *p*-methyl substitution caused a marked intensity increase, suggesting that the transition moment dipole is directed along the line joining the As atom and the para-carbon atom. If the local symmetry of one benzene ring is assumed D_{2h} after para substitution, the polarization of the allowed states of the substituted ring can be deduced from the known symmetry of the benzene states. On para-para-substitution the B_{1u} state (L_a) of the free molecule transforms into an allowed state with para-para polarization. The B_{2u} state (L_b) transforms into a transversely polarized level. The stronger bands are either the ^1L_a benzene analogue bands, red-shifted by mixing with a charge separated state at higher energies (see Fig. 2) or the $(CT)_1$ state which steals its intensity from the transversely polarized B_b state. The above considerations favour the former choice.

This discussion illustrates one more experimental test which may be used to confirm the validity of the theoretical model. According to Fig. 2 there should be two observable spectral bands in the neighborhood of 5·7 eV. The lower energy state is the longitudinally polarized L_a band which is weakened by transference of intensity to $(CT)_2$. The other state is $(CT)_1$ which obtains all of its intensity from the B_b state and thus should appear transversely polarized. If the energy of the zero order CT states is roughly 0·5 eV lower than on Fig. 2 then $(CT)_2$ would be very much weaker than $f = 0{\cdot}12$. The state in the region 5·0–6·0 eV would not be $(CT)_2$ and its intensity

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(6) Ultra-violet Spectral Data, compiled by the American Petroleum Institute Research; Project 44.

(7) E. G. MCRAE and L. GOODMAN, *J. Mol. Spec.* **2**, 464 (1958).

(8) J. R. PLATT, *J. Chem. Phys.* **19**, 263 (1951).

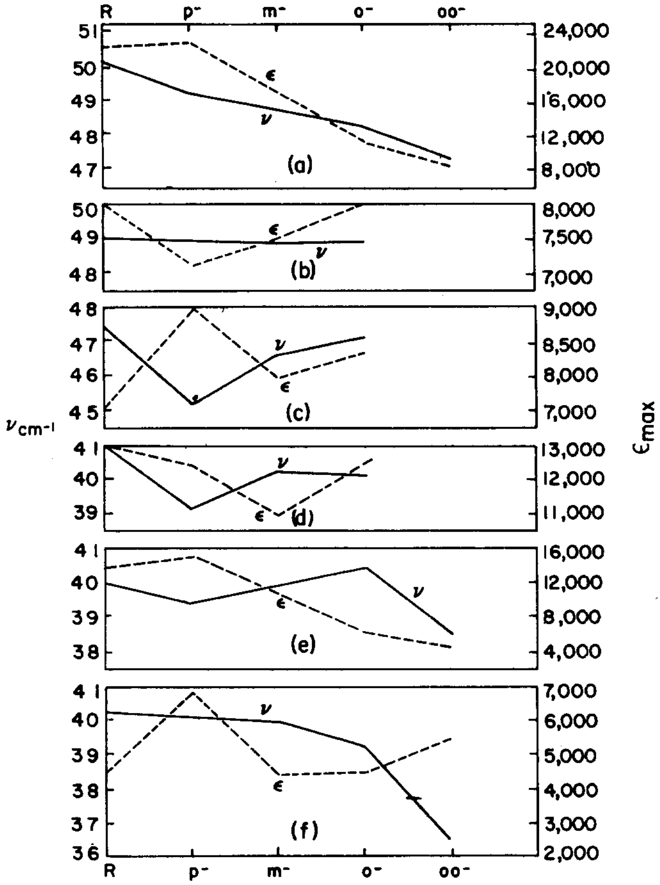

FIG. 7.—Spectral comparisons of intensity and band energy for certain ring methyl substituted phenyl compounds.

(a) N-dimethylaniline: (Reference 9)
(b) fluorobenzene: (Reference 10)
(c) chlorobenzene: (Reference 11)
(d) benzaldehyde: (Reference 12)
(e) N-dimethylaniline: (Reference 9)
(f) triphenylarsine: (Present work)

would derive from L_a and B_a (longitudinally polarized). This is probably the case for the triaryl-derivatives of arsine. Clearly the calculated spectrum is highly sensitive to small changes in the ionization potential of the donor electrons. Thus solvent effects which are known to be derived from specific lone-pair interactions could be utilized to test the model. Such shifts should be accompanied by predictable intensity variations.

Fig. 7 compares the wavenumbers of maximum absorption and the intensities of a few methyl substituted phenyl compounds. The five examples chosen appear to us

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(9) H. B. Klevins and J. R. Platt, *J. Amer. Chem. Soc.* **71**, 1714 (1949).

(10) W. F. Forbes, *Canad. J. Chem.* **37**, 1977 (1959).

(11) W. F. Forbes, *Canad. J. Chem.* **38**, 1104 (1960).

(12) A. Burowoy, *Tetrahedron* **2**, 122 (1958).

to be both precise and representative of a wide variation in ionization potential of the substituent. For some transitions the energy decreases and the intensity increases on paramethyl substitution. The extent of the intensity increase appears to depend on the relative energy of the unshared pair orbital of the substituted atom, being largest for the most easily ionizable lone pair of electrons.

The *o*-methyl and *o,o'*-dimethyl substitution of triphenylarsine, the latter substitution being present in trimesitylarsine, caused a marked reduction of the transition energy and an increase in the intensity. In contrast, *o,o'*-dimethyl substitution of N-dimethylaniline reduces both the intensity and the energy of the charge transfer band(9) depicted in Fig. 7(e).

Energy Variations. The ionization energy of an arsenic lone pair electron will be influenced by replacing a hydrogen atom with a methyl group. Such a substitution will lower the separated (*CT*) state energy and result in a shift of the absorption bands. For example, the 42,160 cm^{-1} *CT* band of aniline is shifted to 40,000 cm^{-1} in N-dimethylaniline.(3,9) Both β and the ionization energy are affected by the methyl group so a detailed interpretation of this shift is difficult. On the other hand, ring hydrogen replacement by methyl should not significantly influence the lone pair ionization energy. For this substitution, the $\pi\pi^*$ state energies will change relative to the (*CT*) states. The resulting spectral shifts may be of different sign and magnitude than the corresponding *LE* shifts (see Fig. 3).

The results in Table 1 show that ring methyl substitution always causes a red shift of the observed spectral band, and an increase of intensity. Unfortunately, without polarization measurements, there is no certainty as to the source of the increased intensity, but in general the methyl substitution must increase the efficiency with which the *CT* states mix the *LE* states in the observed spectral region. As before the manner in which an observed band will shift on ring substitution depends on the relative energies of the non-interacted *CT* and *LE* states. Substitution may conceivably move these states either closer together or farther apart.

Solvent sensitivity. The lone pair orbital energy should be reduced in those solvents which are specifically reactive towards the lone pair as for example in hydrogen bonding solvents. The extent of this stabilization will be considerably less for the excited state in which an electron is partially transferred from the non-bonding orbital. The overall effect of specifically interacting solvents will thus be to increase the energy of the zeroth order *CT* states.

The data of Table 1 shows that the bands were always of higher energies in methanol than in cyclohexane. The 2000 Å band of benzene red shifts under the same change of solvent, as does the 2068 Å band of fluorobenzene,(10) the 2152 Å band of chlorobenzene,(11) and the 2408 Å band of benzaldehyde.(12) This probably means that for these molecules the model of Fig. 2 is inappropriate since the use of slightly higher zeroth order energies for $(CT)_1$ and $(CT)_2$ would result in a blue shift of each of the bands in the region of 5·6 eV. By means of the calibration curve on Fig. 3, the blue shifts from the last column of Table 1 can be shown to correspond to between 1 and 3 kcal/mole of non-bonding orbital stabilization.

CONCLUSIONS

Although the diffuse spectra are too complex for complete characterization the influence of small perturbations by solvent, and ring substituents, is entirely consistent with a charge-transfer description of the bands. The theory predicts two bands whose separation is less than the half-width of the observed spectra, but whose total intensity is comparable with the observed intensity. In certain spectra(1,13) of related materials there is evidence of two bands in the region of 5·6 eV. The calculation given for $(C_6H_5)AsX_2$ is assumed to be applicable to derivatives of $(C_6H_5)_3As$ on the grounds that from the known geometry of such molecules the interactions between the phenyl groups are slight and can be included parametrically in the theory. Such interactions will increase the number of states in a given spectral region but the splitting energies would be too small for observation in the quartz ultra-violet spectral region. The foregoing spectral comparisons are rendered feasible principally because progressive methyl substitutions probably leave the inductive effect, of the heavy atom on the aromatic ring, relatively unaffected.

EXPERIMENTAL

Preparation of the materials

Tri-*m*-tolyl, tri-*p*-tolyl, tri-*p*-xylyl, and trimesitylarsine were prepared by the Wurtz–Fittig reaction using arsenic trichloride, sodium, and the appropriately substituted bromobenzene.(14) Tri-*o*-tolylarsine was prepared by a Grignard reaction using arsenic trichloride and *o*-tolylmagnesium bromide; arsenic tri-iodide was originally used by Burrows and Turner(15) for this preparation. The triphenylarsine used was a recrystallized commercial sample. The uncorrected melting points found for the various compounds are as follows: (*o*-$CH_3C_6H_4)_3As$, m.p. 112° (lit. value 98°); (*m*-$CH_3C_6H_4)_3As$, m.p. 96° (lit. value. 96°); (*p*-$CH_3C_6H_4)_3As$, m.p. 151° (lit. value 145–146°); (*o*,*m′*-$(CH_3)_2C_6H_3)_3As$, m.p. 162° (lit. value 157°); *o*,*o′*,*p*-$(CH_3)_3C_6H_2)_3As$, m.p. 177° (lit. value 170°). As a check on technique the tri-*p*-tolylarsine was analysed: Found: C, 72·2; H, 6·0; As, 21·5; mol. wt, 345. Calc. for $C_{21}H_{21}As$: C, 72·4; H, 6·0; As, 21·6%; mol. wt., 348. The infra-red spectra of these and related compounds will be published later.

The electronic absorption spectra were recorded on the Cary model 14 Spectrophotometer. The lower wavelength limit of this instrument was 2050 Å as determined by our solvent absorption. The solvents were spectroscopic grade methyl alcohol or cyclohexane.

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(13) W. R. Cullen, Unpublished research.

(14) A. Michaelis, *Ann.* **321,** 141 (1902).

(15) G. J. Burrows and E. E. Turner, *J. Chem. Soc.* 1373 (1920).