negative ΔS° and small negative ΔH° are characteristic in these cases.

The quantity of primary interest is the large negative ΔS°. Partial ordering of the solvent by the strong solvation of sodium ions in monomer ketyl could be primarily responsible for this change. The solvation of sodium ion in the ethereal solvent has been considered to be one of the main causes of the large entropy change in the dissociation of sodium naphthalenide ion pair.[21] Mathias and Warhust[20] also mentioned the decrease in the solvent entropy due to the solvation in rationalizing a decreased value of the pre-exponential factor for the reaction of monosodium fluorenone and methyl iodide. Qualitatively this will be understood in the following way. As discussed in the previous section, two sodium ions are surrounded by two large ketyl anions and the solvation is greatly hindered in the paramagnetic dimer, while in the monomer more space is accessible for solvent molecules. The relative difference in the solvent ordering in the monomer and the dimer would result in the negative ΔS° for the dissociation. The small negative ΔH° would come mainly from the difference of two competing electrostatic interactions, namely, electrostatic interaction between positive ions and aromatic negative ions and that of solvation.

The dissociation constants increase as the size of the positive ion increases. The weakened electrostatic interaction between the positive ion and the negative charge of the ketyl and also the solvent molecules would weaken the solvation as well as the force which combines two ketyls. Dimers are predominant in aliphatic ketyls. This may be accounted for by the stronger electrostatic interaction due to the more localized charge on the carbonyl group.

While the equilibrium between the paramagnetic monomer and dimer is the major equilibrium in dilute ether solution, such as DME, THF, and Me THF, the major equilibrium in nonpolar solvents is the one between the paramagnetic and the diamagnetic dimer.

[21] N. A. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 133 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT STONY BROOK, STONY BROOK, L. I., N. Y.]

π-Complex Interactions. II.[1] Methyl Substituted Benzenes and Naphthalenes with Tetracyanoethylene[2]

BY ARTHUR R. LEPLEY

RECEIVED DECEMBER 23, 1963

The charge-transfer spectra of the π-complexes formed by a number of methyl substituted benzenes and naphthalenes with tetracyanoethylene have been measured. Comparison of the observed energy shifts with other spectroscopic shifts and energy level correlations shows that these π-complexes can be reasonably interpreted in terms of first-order pertubation theory using only inductive effects. The highest occupied Hückel molecular orbital relationship previously established for alternant and nonalternant hydrocarbons is used in evaluating the coulomb pertubation parameter for methyl shifts.

Introduction

A simple molecular orbital (MO) treatment has previously been successfully applied to the charge-transfer spectra of alternant[3,4] and nonalternant[1] hydrocarbons. These hydrocarbons (D) containing only sp^2-carbon atoms donate electrons from their highest occupied orbital (h.o.o.) to an interacting acceptor molecule (A) where it enters the lowest unoccupied orbital (l.u.o.). The energy, E_π, required for this transition is thus proportional to the difference in orbital energies m (eq. 1)

$$E_\pi = m_{A1^*} - m_{D1} \qquad (1)$$

where the subscripts denote the molecule and the energy levels, numbering from the h.o.o. and l.u.o. (*), respectively. The individual orbital energies from the Hückel MO treatment are given by $\alpha + x_i\beta$. Here α and β are, respectively, the coulomb and exchange integrals. Since the hydrocarbons contribute only p-orbitals from sp^2-carbon atoms to the energy matrix, the x_i and relative m_{D1} may be determined.[5]

The calculated x_i's for the donor molecules have been used to determine the parameters $m_{A1}*$ for the acceptors p-benzoquinone,[6] chloranil,[6] iodine,[5] tetracyanoethylene,[4] tetracyanoquinodimethane,[6] trinitrobenzene,[3,6] and trinitrofluorenone.[1] An example of such evaluation gives the relationship between E_π and x_1 for tetracyanoethylene (eq. 2)

$$x_{D1} = (E_\pi - 0.34)/3.06 \qquad (2)$$

where E_π is in electron volts and x_{D1} is dimensionless.

In their classic work relating ionization potentials to the frequency of charge-transfer iodine complexes, McConnell, Ham, and Platt[7] included a wide range of aromatic compounds. Among these were a number of methyl substituted aromatics. The general nature of the inclusion of such compounds has been adequately documented[8,9] for a variety of acceptors. However, no attempt has been made to make specific comparisons of the influence of this group on the charge-transfer process.

The ionization potential relationship to methyl substituents has been explored.[10] The MO h.o.o. which correlate[11] with the ionization potential has been used[10]

[1] Part I: A. R. Lepley, *J. Am. Chem. Soc.*, **84**, 3577 (1962).

[2] Presented in part before the Division of Physical Chemistry, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 22, 1964, Abstracts, p. 32D.

[3] M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961).

[4] M. J. S. Dewar and H. Rogers, *ibid.*, **84**, 395 (1962).

[5] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

[6] R. Beukers and A. Szent-Gyorgyi, *Rec. trav. chim.*, **81**, 255 (1962).

[7] H. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[8] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, Germany, 1961.

[9] R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

[10] A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

[11] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1950).

TABLE I

EFFECT OF METHYL SUBSTITUENTS IN BENZENE ON THE LONG WAVE LENGTH CHARGE-TRANSFER ENERGY

Subst. pos.	λ_{M+P},[a] mμ	λ_π, mμ	λ_2, mμ	$-\Delta E_\pi$, e.v.	$\sum_n \sum_r c_{1r}^2 / n$	x_{1Me}[b]
0	384	388 ± 2		(3.32)		(1.00)[c]
1	406	414 ± 2		0.20	0.333	0.87
1,2	430	439 ± 2		.37	.500	.81
1,3	440	441 ± 2		.38	.500	.81
1,4	460	461 ± 10	415[a]	.50	.667	.77
1,2,3		465 ± 2		.53	.667	.76
1,2,4		470 ± 10		.56	.777	.75
1,3,5	461	466 ± 2		.54	.667	.76
1,2,3,5		484 ± 2		.64	.917	.73
1,2,4,5	480	500 ± 10[d]	455 ± 15[d]	.72	1.000	.70
1–5	520	516 ± 2		.80	1.133	.68
1–6	545	544 ± 2		.91	1.333	.63

[a] Ref. 13. [b] Calcd. from eq. 2. [c] Ref. 16. [d] Estimated for unresolved peaks.

to explore the shifts in coulomb and exchange parameters for several substitution models. The states for the donor molecule in π-complex excitation should be comparable to those of a molecule in the ionization process as shown previously.[7–9] A test of this generalization would be determined from the charge-transfer–h.o.o. relationship for a set of methyl substituted aromatics. This evaluation of ground state levels for the methyl group, particularly in a simple inductive model,[12] might thus allow comparison with other empirically determined parameters.

Although many methyl substituted aromatics are known, the extent of multiple group substitution can be most broadly observed in methylbenzenes. The degeneracy in the parent system, however, sometimes raises questions on the generality of any treatment including only this system. Therefore, a study of both methyl substituted naphthalenes and benzenes was made.

The parent molecules, particularly benzene, do not give easily determined charge-transfer bands with most acceptors. However, the limited reactivity of benzene and naphthalene toward Diels–Alder addition suggested the use of tetracyanoethylene (TCNE) as the acceptor. Appreciable shifts for several methyl benzenes have been observed with TCNE.[13] These earlier measurements[13] have been compared with those of the present study.

Experimental

Materials.—The methyl substituted benzenes and naphthalenes were used as supplied by Eastman Kodak, Aldrich Chemical Co., and K & K Laboratories. These materials all showed single major peaks (>90%) with gas chromatography and had m.p.'s in agreement with the literature. Tetracyanoethylene was used as supplied without further purification. The chloroform for spectroscopic measurements was Eastman Kodak Spectrograde.

Spectroscopic Measurements.—Equal volumes of tetracyanoethylene (0.005 *M*) in chloroform and the donor solution were used to prepare the complexes. All donor solutions were 0.05 *M* in chloroform. A Cary Model 14 spectrophotometer and/or Perkin–Elmer Model 202 spectrophotometer were used for all measurements. Calibration of the two instruments was accomplished using the visible bands of azulene[14] in 2,2,4-trimethylpentane. Spectra were measured in 1.0-cm. cells in the range 340–750 mμ. When absorption was still appreciable at 750 mμ the region out to 1100 mμ was scanned.

TABLE II

EFFECT OF METHYL SUBSTITUENTS IN NAPHTHALENE ON THE LONG WAVE LENGTH CHARGE-TRANSFER ENERGY

Subst. pos.	Obsd. max.,[a] mμ λ_π	Obsd. max.,[a] mμ λ_2	Gaussian max., mμ λ'_π	Gaussian max., mμ λ'_2	$-\Delta E_\pi$, e.v.	Σc_{1r}^2	x_{1Me}[b]
0	555[c]	431[c]	559	427	(2.22)		(0.618)[d]
1	592	440	593	438	0.12	0.181	.57
2	579	458	585	454	.10	.069	.58
1,2	613	463	615	458	.20	.250	.55
1,3	607	465	614	461	.19	.250	.55
1,4	624	445	625	441	.23	.362	.54
1,5	622	444[e]	624	442[e]	.23	.362	.54
1,6	610	466	616	462	.20	.250	.55
1,8	635	438	635	432	.26	.362	.53
2,3	598	490	613	489	.19	.138	.55
2,6	606	479	617	476	.21	.138	.55
2,7	598	491	616	489	.20	.138	.55
2,3,5	632	495	638	491	.27	.319	.53
2,3,6	625	526	645	519	.29	.207	.52

[a] Assignment error ±2 mμ estimated for all values. [b] Calcd. from eq. 2. [c] 560 and 429 mμ; ref. 13. [d] Ref. 16. [e] λ_3 obsd. max. 355 mμ, Gaussian max. 354 mμ.

Calculations.—All computations were made in the University computer center using an IBM 1620 with 60,000 memory units. Programs written by the author in FORTRAN and used in this work include an iterative multiple Gaussian fit for spectra and least squares correlation routines.

Results

Table I lists the wave lengths (λ_π) with their uncertainties, the energy shift ($-\Delta E_\pi$), the coulombic perturbation coefficients ($\sum_n \sum_r c_{1r}^2/n$), and the empirical orbital coefficients (x_{1Me}) for eleven methyl substituted benzenes and the parent hydrocarbon. These values plus those for the second charge-transfer absorption maxima (λ_2), and the computed Gaussian curve fit maxima (λ_π' and λ_2') are given for naphthalene and thirteen methylnaphthalenes in Table II.

The TCNE complex bands were well separated from absorption wave lengths of either the donor or acceptor and had the broad shape characteristic of charge-transfer absorption. In addition to the long wave length band, several compounds had similar bands at shorter wave lengths.[13] These bands, λ_2, were of the same relative intensity as the long wave length bands but were not readily correlated with MO quantities. The broad shape of the charge-transfer band prevents extremely accurate measurement of peak maxima. This gives rise to the assignment errors shown, Tables I and II. Where two peaks were observed, the absorption maxima location changed with peak overlap. This distortion increases with decreasing separation of λ_π and λ_2. Therefore the absorption curves of naphthalene and the methyl substituted naphthalenes were treated by a computer curve fitting technique.

The charge-transfer bands were assumed to have a Gaussian distribution and to be additive. The first term in the Taylor series for variation of the band maximum locations and band widths at half-height was used in the Newton–Raphson method. The observed maxima were initial estimates of band locations in this iterative least squares fit. In general the method converged to six significant figure accuracy in less than eight iterative cycles. The band maxima for Gaussian fit were in good agreement with the method of maximum slope,[15] even when the absorption difference be-

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(12) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

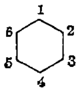
(13) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

(14) P. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910 (1947).

(15) Extrapolation of the maximum slope on either side of each observed absorption peak gives a reasonable value for the band maximum at the point of intersection. When the Gaussian fit diverged using observed maxima, the maximum slope method gave values for rapid convergence.

tween band maxima and the intervening minimum was small (*cf.* 2,7- and 2,3,6-substituted naphthalenes). The values are in excellent agreement for the TCNE complexes in chloroform and in methylene chloride.[13]

The coulombic perturbation coefficients $\sum_n\sum_r c_{1r}^2/n$ were calculated from values in a recent compilation[16] using the values for the h.o.o. In the naphthalenes, no ambiguity occurs using the simpler form of the coefficient $\sum_r c_{1r}^2$ where r is the location of substituent groups. However, since the choice of the initial position in benzene defines the coefficients summed, the mean over the n equivalent structures was used. Furthermore, since the energy levels of benzene are degenerate, the mean of these two c_{12}^2 values was used with the c_{11}^2 which is antisymmetric with respect to its in-plane perpendicular axis but symmetric with respect to its in-plane parallel axis. The case of 1,2,4-trimethylbenzene exemplifies the nonidentity of structures. If the numbering with position 1 at the top of the structure I is used, the three structures II, III, and IV are obtained by choosing each substituent in turn at the 1-position and maintaining a minimum in summing the position numbers.[17] Since the contribution of the 1- and 2-positions is not identical for c_{1r}^2 and since 1 = 4 and 2 = 3 = 4 = 5 for c_{1r}^2, the number of positions equivalent to 1 and/or 2 is summed for each structure. Structures II and IV both have $2c_{11}^2 + c_{12}^2$, while structure III has $c_{11}^2 + 2c_{12}^2$. However, the molecule behaves as if it had only one structure which is a composite of II, III, and IV. The calculated $\sum_n\sum_r c_{1r}^2/n$ values are therefore a linear combination of all structures normalized to one active structure.



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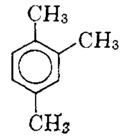
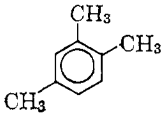
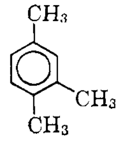


II



III



IV

The charge-transfer energy level shifts, $-\Delta E_\pi$, are plotted against the coulomb perturbation coefficients in Fig. 1. The scatter in this plot is quite reasonable by comparison with the deviation in the AH *vs.* x_1 plot.[4]

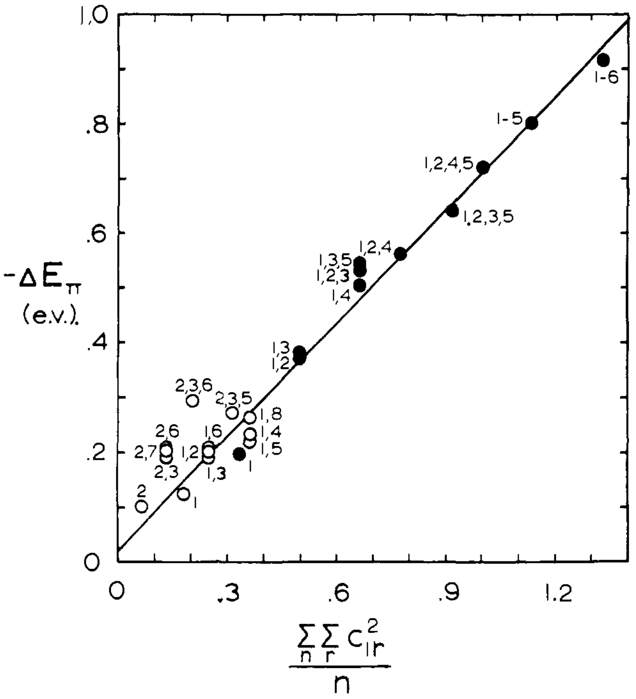


Fig. 1.—Plot of the shift in the charge-transfer long wave length absorption maxima against $\sum_r c_{1r}^2$ for ●, methylbenzenes and, ○, methylnaphthalenes. Numbers refer to the location of substituents.

Discussion

Streitwieser and Schwager[18] have shown that the addition of methyl substituents to naphthalene results in an increase in the reduction potential, $E_{1/2\text{ red}}$ (eq. 3).

$$x_{1^*} = (E_{1/2\text{red}} + 0.396)/2.41 \qquad (3)$$

This change corresponds to an increase in the l.u.o. coefficient, eq. 4, where the letters in the subscripts correspond to the parent alternant hydrocarbon (AH) molecule and the methyl (Me) substituted molecule.

$$x_{1^*\text{Me}} > x_{1^*\text{AH}} \qquad (4)$$

This increase is in opposition to the shift on increasing the extent of the parent conjugated system. Thus, for example, benzene has a larger value of x_{1^*} than naphthalene.

The oxidation potentials[19] for methyl aromatics are lower than those of the parent hydrocarbon. The energy h.o.o. relationship was given as

$$x_1 = (E_{1/2\text{ox}} - 0.19)/2.13 \qquad (5)$$

The lower energy of the methyl compounds requires a decrease in the h.o.o. coefficient, eq. 6.

$$x_{1\text{Me}} < x_{1\text{AH}} \qquad (6)$$

The methyl oxidation shift parallels that of parent conjugation extension.

The charge-transfer band from eq. 2 and 6 would thus be shifted toward lower energies and correspondingly longer wave lengths. The results, Tables I and II, are in agreement with this qualitative requirement. These measured energies are correlated with relative energy levels from simple MO calculations. The calculations give equal but opposite values for the h.o.o. and l.u.o. coefficients in AH's. The parent hydrocarbon levels are symmetric with respect to the value of the coulomb integral, Fig. 2. The relative parent levels are

$$x_{1\text{AH}} = -x_{1^*\text{AH}} \qquad (7)$$

Thus eq. 4, 6, and 7 indicate that the h.o.o. coefficient undergoes a greater shift than the l.u.o. coefficient. The last conclusion is further emphasized by the energy decreases[20] in the p-band[21] of the methyl substituted compounds relative to the parent. The spectroscopic

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(16) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," 2nd Ed., Mathematical Institute, Oxford, England, and the Center de Mecanique Ondulatoire Applique, Paris, France, 1959.

(17) A mirror image set of three additional structures may also be obtained, but these are not distinct for the present argument.

(18) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

(19) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

(20) J. Petruska, *J. Chem. Phys.*, **34**, 1120 (1961).

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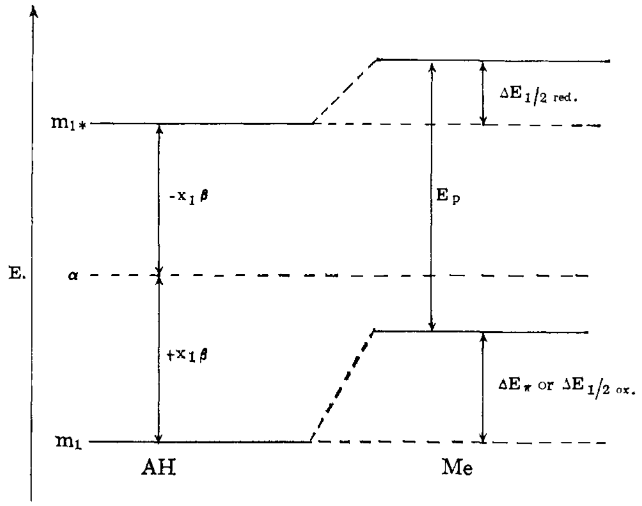

Fig. 2.—Energy level diagram for the shifts on methyl substitution for the alternant hydrocarbons (AH), showing the energy levels for the ground, m_1, and excited, $m_1{}^*$, states in terms of the coulomb integral, α, and the resonance integral, β. The relationship of these levels to the shifts in the oxidation, $^1/_2$ox, reduction, $^1/_2$red, and charge-transfer band, π, energies are shown. The spectroscopic *para* band transition, p, correlation with energy levels is indicated.

energy, E_p, has been correlated[22] with the transfer of an electron from the h.o.o. to the l.u.o., eq. 8.

$$x_1 - x_{1^*} = (E_p - 1.30)/2.36 \qquad (8)$$

The decrease in E_p on methyl substitution indicates that the energy level transfer shows a decreasing difference in a methylated species, eq. 9

$$\Delta x_{(1-1^*)\mathrm{Me}} < \Delta x_{(1-1^*)\mathrm{AH}} \qquad (9)$$

where the variation in x, Δx, is given by the subscribed levels, *i.e.*, $\Delta x_{(1-1^*)} = x_1 - x_{1^*}$. The parent spectroscopic shift Δx_{AH} from eq. 7 gives $2x_1$. Agreement in the ratio of 1:2 between Δx_{AH} and x_1 has been shown[1] for trinitrofluorenone π-complexes. The relationships from eq. 4, 7, and 9 are thus equivalent to those of 4, 6, and 7 confirming the greater shift in the h.o.o. coefficients, eq. 10

$$\Delta x_{(1\mathrm{AH}-1\mathrm{Me})} > \Delta x_{(1^*\mathrm{Me}-1^*\mathrm{AH})} \qquad (10)$$

even though the absolute values of $x_{1\mathrm{Me}} < x_{1^*\mathrm{Me}}$. The energy level diagram, Fig. 2, illustrates the relative changes in the calculated levels necessary to account for the empirical energies.

The effect of methyl substituent in calculations might, on the basis of the above discussion, be determined by complete evaluation of the $m_{1\mathrm{D}}$ changes in eq. 1 for parent and substituted compound. Equation 2 was obtained from eq. 11

$$E_\pi = m_{1^*\mathrm{A}} - \alpha - x_1\beta \qquad (11)$$

for the AH's. Variation of the coulomb integral α and the resonance integral β are allowed[23] by eq. 12 and 13.

$$\alpha_{\mathrm{Me}} = \alpha_{\mathrm{AH}} + h\beta_{\mathrm{AH}} \qquad (12)$$

$$\beta_{\mathrm{Me}} = k\beta_{\mathrm{AH}} \qquad (13)$$

The values of h and k are necessary to complete the determination for the methyl substituted compounds. The evaluation of these parameters would be simplified if only one of the variables were important, *i.e.*, if $h = 0$ or $k = 1$.

Comparison of the energy level relationships (eq. 4, 6, 7, 9, and 10) with other treatments of methyl compounds suggests that a single parameter might be adequate. The transition energy, E_p, has been[24] quantitatively considered using pertubation theory.[25] A first-order development of this method should suffice for our purposes. The shift in energy on perturbation was given in terms of a Taylor series in α and β. The first-order terms are given in eq. 14.

$$\delta m = \frac{\partial m}{\partial \alpha}\delta\alpha + \frac{\partial m}{\partial \beta}\delta\beta \qquad (14)$$

Using the model of Wheland and Pauling,[12] only atomic orbitals (AO) of the parent AH were used in evaluation of the partial derivatives. Furthermore, it was assumed that only the AO at the point of methyl attachment was appreciably effected by the perturbation.[26] The partial derivatives[25] were therefore given by the AO coefficients, c

$$\frac{\partial m_{\mathrm{i}}}{\partial \alpha} = \sum_{\mathrm{r}} c_{\mathrm{ir}}{}^2; \quad \frac{\partial m_{\mathrm{i}}}{\partial \beta} = \sum\sum_{\mathrm{r}\neq\mathrm{s}} c_{\mathrm{ir}}c_{\mathrm{is}}$$

where the r indicates the parent AO of substitution and the s is an adjacent bonding AO. Rewriting eq. 14 in terms of the partials and $\delta\alpha$ and $\delta\beta$ from eq. 12 and 13, respectively, gives eq. 15

$$\Delta m_{\mathrm{i}} = \sum_{\mathrm{r}} c_{\mathrm{ir}}{}^2 h\beta + \sum\sum_{\mathrm{r}\neq\mathrm{s}} c_{\mathrm{ir}}c_{\mathrm{is}}(k-1)\beta \qquad (15)$$

where β is β_{AH}. The shift in charge-transfer bands on methyl substitution from eq. 1 gives

$$\Delta E_\pi = E_{\pi\mathrm{Me}} - E_{\pi\mathrm{AH}} = m_{1\mathrm{AH}} - m_{1\mathrm{Me}} = -\Delta m_1$$

The observed energy shifts may to a first approximation[25] be constructed from a coulombic or inductive term, I, and a resonance or exchange term, E, the first and second terms of eq. 15, respectively. The electron density, q_{r}, at atom r in the AH is calculated[27] from the AO coefficients of the occupied orbitals, eq. 16

$$q_{\mathrm{r}} = \sum_{\mathrm{i}} n_{\mathrm{i}} c_{\mathrm{ir}}{}^2 \qquad (16)$$

where i denotes the energy level and n the orbital occupancy. The q_{r} is changed if a perturbation shifts the AO coefficients. The change, Δq_{r}, related to the observed substituent model is $hc_{\mathrm{ir}}{}^2$. This local q_{r} variation is principally electrostatic or inductive.[25] The $\sum_{\mathrm{r}} c_{\mathrm{ir}}{}^2 h$ term in eq. 15 is associated with $\sum_{\mathrm{r}} \Delta q_{\mathrm{r}}$. Since the variation in the coulomb integral on substitution, h (eq. 12), and the Δq_{r} are basically electrostatic, the I effect is associated with the first term of eq. 15.

The second term in eq. 15 has similarly been shown[25] to be related to the bond order, $p_{\mathrm{rs}} = \sum_{\mathrm{i}} nc_{\mathrm{ir}}c_{\mathrm{is}}$. The p_{rs} change on perturbation is $\Delta p_{\mathrm{rs}} \approx dc_{\mathrm{ir}}c_{\mathrm{is}}$, where $d = k - 1$. The individual effects between pairs of bonded atoms,

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(22) *Cf.* ref. 5, Chapter 8.

(23) Reference 5, Chapter 4.

(24) D. Peters, *J. Chem. Soc.*, 646 (1957).

(25) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947); **A193**, 447, 456 (1948); **A195**, 188 (1948).

(26) The methyl shifts observed were relatively small and so closely related to the properties of the parent AH that inclusion of additional parameters specifically related to the methyl group did not seem justified. *Cf.* R. S. Mulliken, C. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(27) Reference 5, Chapter 2.

one of which is perturbed, and the cumulative effect in the molecule are principally resonance terms, E.

The p-band shifts have been shown[24,28] to be principally accounted for by E. The difference between the reduction potential shifts and the p-band shifts results in an essentially pure I term. The latter is in agreement with a simple inductive treatment of ionization potentials on methyl substitution.[29] Therefore the charge-transfer bands should be amenable to consideration using only the I term.

The plot of ΔE_π *vs.* $\Sigma c_{\text{ir}}{}^2$ in Fig. 1 shows scatter similar to that[4] for the AH–TCNE E_π *vs.* x_1. The least squares fit of the points in Fig. 1 to a straight line also passes near the origin. Therefore, a single parameter, h, was evaluated. The slope, t, of Fig. 1 is seen from eq. 15 to equal $h\beta$ since $k = 1$. The coulomb integral used for the $x_{1\text{AH}}$ *vs.* E_π proportionality was -3.06 e.v.[4] The value for the inductive perturbation parameter is therefore

$$h = -0.21$$

The negative sign of this coefficient is required by the earlier qualitative treatment and Fig. 1. This value is in excellent agreement with other recent treatments ($h = -0.21$ from reduction potentials).[18]

The MO coefficients $x_{1\text{Me}}$ for the h.o.o. may be determined directly from eq. 2. This is in agreement with the inclusion of methyl aromatics in the ionization potential, charge-transfer relationship.[7,8] The $x_{1\text{Me}}$ values in Tables I and II are inversely related to the coulomb perturbation coefficients, eq. 2 and 15. The perturbation model used for determination of h is, however, not explicit in the $x_{1\text{Me}}$ values.

The perturbation parameter determined may be used to calculate directly the $x_{1\text{Me}}$ for AH compounds using the Hückel MO method. Calculations for comparison with the semiempirical h.o.o. coefficients are currently in progress.

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[28] C. A. Coulson, *Proc. Phys. Soc.* (London), **A65**, 933 (1952); H. C. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.*, 1404 (1952).

[29] A. Streitwieser, Jr., *J. Phys. Chem.*, **66**, 368 (1962).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

Evidence for a Cooperative Intramolecular Transition in Poly-L-proline

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The specific rotation of poly-L-proline was measured in solvent mixtures of glacial acetic acid and 1-propanol. After proper allowance for time-dependent mutarotations, an abrupt decrease in the equilibrium levorotatory power of these solutions was observed to occur (with increasing alcoholic content) in the solvent composition interval 50–60% alcohol. It was also shown that a corresponding crystallographic transition occurs among equilibrated poly-L-proline samples removed from solution in the vicinity of this narrow solvent composition interval, this transition also being accompanied by the appearance of several infrared absorption bands. These results offer additional verification for the previously reported occurrence of the reversible intramolecular interconversion of two crystallographically distinct forms of poly-L-proline. The present study demonstrates for the first time the cooperative nature of the transition.

Ever since its synthesis almost a decade ago,[2] poly-L-proline has attracted the continuing interest of several groups of investigators. In large part this interest has centered on diverse observations leading to the now widely accepted view that poly-L-proline may exist in either of two configurational forms differing markedly in their solution properties as well as in their crystallographic structures. Early evidence for such dimorphism was noted by Kurtz, Berger, and Katchalski[3] who observed that, as obtained from its polymerizing mixture, poly-L-proline is water insoluble and slightly dextrorotatory. When this form, which is designated I, is dissolved in aliphatic acids, it proceeds to mutarotate slowly (*i.e.*, for many days) to a water-soluble highly levorotatory form designated II.

Subsequent investigations have shown that forms I and II are further distinguished by differences in optical rotatory dispersion,[4,5] hydrodynamic properties,[4] and absorption spectra, both in the infrared[5,6] and in the ultraviolet[7] regions of the spectrum. It has also been shown that the two forms are chemically indistinguishable[3] and that the back mutarotation II → I may be effected by the dilution of acid solutions of form II with large excesses of aliphatic alcohols.[6] Thus the two forms may be interconverted in a completely reversible manner, the kinetics of both the forward and back mutarotations also having been studied. In this connection, we note that in their study of the forward (I → II) mutarotation of dilute poly-L-proline in glacial acetic acid Downie and Randall[8] reported an activation energy of 22.9 kcal./mole of prolyl residue and that Steinberg, Harrington, Berger, Sela, and Katchalski[9] reported a value of 20.6 kcal./mole for the same process and 20.2 kcal./mole for the reverse mutarotation (II → I) in a solvent consisting of a 1:9 (v./v.) mixture of acetic acid and 1-propanol.

When one couples these observations with calculated values of about 21 kcal. per mole for the resonance en-

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