Optically Active Aromatic Chromophores. III.[1] A Remote Optically Active Phenyl Ring

Sir:

The question of whether a monosubstituted benzene ring could exhibit optical activity was answered recently by observations of weak Cotton effects in the ORD curves of several benzene derivatives having a phenyl group directly at or one carbon removed from the asymmetric center.[2] The relatively weak Cotton effects observed in the 260-mμ region are associated with the symmetry-forbidden $\pi-\pi^*$ transition of the aromatic ring. Moscowitz and co-workers[2a] pointed out that previous failures to observe aromatic Cotton effects in open-chain benzene derivatives were not a question of kind but of degree of optical activity.

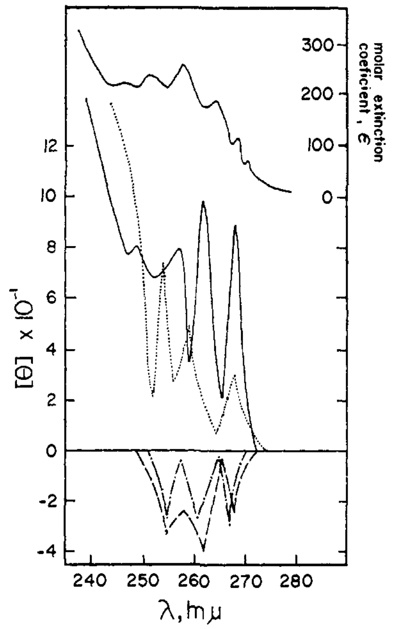
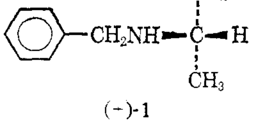


Figure 1. Isotropic absorption spectrum of L-(+)-2-(N-benzylamino)propanol-1, (+)-**1**, in heptane solution. Circular dichroism spectra of (+)-**1**, in ——— heptane, ······ acetonitrile, —·— 0.1 *N* HCl, and - - - - 95% ethanol-5% 0.1 *N* HCl solution.

We wish to present evidence for an optically active monosubstituted benzene ring which is separated from the asymmetric center by two atoms, one of them a heteroatom. In addition, the data bear on the current problem of correlation of absolute configuration with the sign of an appropriate Cotton effect in open-chain systems.

The isotropic absorption spectrum and circular dichroism spectra of L-(+)-2-(N-benzylamino)propanol-1, (+)-**1**, in four solvents are shown in Figure 1.



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In all solvents examined[3] a Cotton effect was observed in the CD spectrum in the 260-mμ region, corresponding to a band containing fine structure in the isotropic absorption spectrum. Although this aromatic Cotton effect is quite weak,[4] it is readily discernible in the CD spectrum because of the absence of background effects such as are found in ORD measurements.

The 260-mμ Cotton effect in the CD spectrum of (+)-**1** is positive in the case of the free amine (acetonitrile and heptane solutions) and, as expected, the magnitude is increased on going to the more nonpolar solvent (Figure 1). However, in the case of the hydrochloride the sign of the Cotton effect is inverted.

Introduction of a formal positive charge on nitrogen is not expected to result in inversion of the Cotton effect based on pH-dependence studies of the CD spectra of open-chain amines.[5]

On the basis of CD studies of open-chain systems,[6] the inversion of the aromatic Cotton effect of (+)-**1** is most consistently interpreted as due to a shift in the conformational equilibrium of this freely rotating system upon protonation of the nitrogen atom.[7] The observed Cotton effect is the resultant of the Cotton effects associated with each rotameric species in solution. Every conformation possesses a contribution to the observed Cotton effect which varies in sign and in amplitude from conformer to conformer. Thus, the measured Cotton effect is sensitive to the relative proportions of rotamers present.[8]

The solvent-dependent Cotton effect found in this work illustrates that caution must be used in the important work of correlating absolute configuration with the sign of an appropriate Cotton effect in conformationally mobile systems.

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[1] Part II: L. Verbit, S. Mitsui, and Y. Senda, *Tetrahedron*, **22**, 753 (1966).

[2] (a) A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Am. Chem. Soc.*, 87, 1813 (1965); (b) L. Verbit, *ibid.*, **87**, 1617 (1965); (c) ref 1.

[3] Other solvents used but not reported due to space limitation were water, 1,2-dimethoxyethane, and absolute ethanol. The aromatic Cotton effect in the 260-mμ region was positive in these solvents.

[4] A JASCO Model ORD/UV/CD-5 instrument with a sensitivity of 2×10^{-5} ΔA in the CD mode was used.

[5] L. Verbit and P. J. Heffron, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract C167.

[6] Reference 5, Abstract S169.

[7] An alternative explanation for the observed inversion of sign is the mixing of a nitrogen transition with a transition of the aromatic ring. Such mixing would be much less important in the σ-bonded protonated nitrogen. Variable-temperature and nitrogen-substitution experiments are planned in order to obtain more direct evidence of the origin of the Cotton effect inversion.

[8] W. S. Briggs and C. Djerassi, *Tetrahedron*, **21**, 3455 (1965).

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Chemical Shifts of Boron-11 in Icosahedral Carboranes

Sir:

In view of the difficulties in applying the general theory[1] of chemical shifts to large molecules, we have

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[1] R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb, *J. Chem. Phys.*, 38, 550 (1963).

turned to relationships found[2-4] for ^{13}C, ^{14}N, and ^{19}F nmr shifts and ground-state molecular wave functions in order to extend theories of ^{11}B chemical shifts beyond their present limits, which are to derivatives of BH_3. This is an attempt also to go beyond correlations with electronegativities,[5] Hammett constants,[6] and π densities.[4b] The present study was prompted by the discovery that ^{11}B chemical shifts in o-$B_{10}C_2H_{12}$ moved downfield[7] with increasing negative charge (as suggested by molecular-orbital studies, the inductive rule,[8] and sequential substitution), and by the even more surprising prediction[9] that the isolated BH unit is paramagnetic even though $^1\Sigma$.

These indications, together with an estimated upper limit of 1 ppm for differences in the boron shieldings due to ring currents, have led us to calculate the probable large paramagnetic contributions to the ^{11}B shift in the three icosahedral carboranes: o-, m-, and p-$B_{10}C_2H_{12}$. This closely related set of compounds should allow approximate constancy in the average energy approximation. We have included electrons in 2p orbitals, both for the nucleus under consideration and for bonds to all other atoms, and estimated the diamagnetic contributions.

The diamagnetic shielding[4a] averaged over all orientations is

$$\sigma^{(d)} = \frac{\alpha}{3}\sum_{a=1}^{m}\sum_{b=1}^{m} P_{ab}\langle r^{-1}\rangle_{ab} \tag{1}$$

where the P_{ab}'s are the elements of the usual charge–bond order matrix over all orbitals a and b on center A. Following Pople's notation,[2c] we find the corresponding expression for the paramagnetic shielding

$$\sigma^{(p)} = -\frac{\alpha^2}{2\Delta E}\langle r^{-3}\rangle_{2p}(Q_{AA} + \sum_{A\neq B} Q_{AB}) = -\frac{19.5}{\Delta E}(Q_{AA} + \sum_{A\neq B} Q_{AB}) \tag{2}$$

where

$$Q_{AA} = {}^4/_3[(P_{x_Ax_A} + P_{y_Ay_A} + P_{z_Az_A}) - {}^1/_2(P_{x_Ax_A}P_{y_Ay_A} + P_{y_Ay_A}P_{z_Az_A} + P_{z_Az_A}P_{x_Ax_A}) + {}^1/_2(P_{x_Ay_A}{}^2 + P_{y_Az_A}{}^2 + P_{z_Ax_A}{}^2)] \tag{3}$$

$$Q_{AB} = {}^2/_3[-(P_{x_Ax_B}P_{y_Ay_B} + P_{y_Ay_B}P_{z_Az_B} + P_{z_Az_B}P_{x_Ax_B}) + (P_{x_Ay_B}P_{y_Ax_B} + P_{y_Az_B}P_{z_Ay_B} + P_{z_Ax_B}P_{x_Az_B})] \tag{4}$$

α is the fine structure constant, and the one-center integral $\langle r^{-3}\rangle_{2p}$ has the value $K^3/3$, where K is the value of the Slater 2p exponent for boron. When the mean excitation energy ΔE is in atomic units (au), $\sigma^{(p)}$ will be in parts per million.

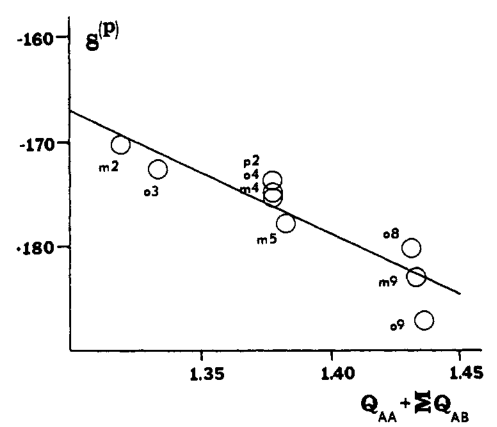

Figure 1. Plot of observed chemical shifts after diamagnetic correction *vs.* $Q_{AA} + \Sigma Q_{AB}$ for the three carborane isomers. The equation of the least-squares line is $\delta^{calcd} - \sigma^{(d)} = -12.4 - 118.9(Q_{AA} + \Sigma Q_{AB})$. For atom labels see Table I.

Procedures and suitable parameters[10a] for calculating boron hydride wave functions have been extended to carboranes, using SCF results[11] for diborane and ethane. Matrix elements between 2s and 2p orbitals on the same center[10a] are neglected here, but their inclusion leaves the results substantially unchanged.[12]

In Table I we show values of Q_{AA}, ΣQ_{AB}, and $\sigma^{(d)}$ for the unique atoms of the three isomers of $B_{10}C_2H_{12}$. In Figure 1 the diamagnetically corrected values of the chemical shift ($\delta^{(p)} = \delta^{obsd} - \sigma^{(d)}$) are plotted against the quantity $Q_{AA} + \Sigma Q_{AB}$; the least-squares line drawn through the points gives a mean excitation energy of 0.164 au (4.5 ev). We note that the changes in $\sigma^{(d)}$ from atom to atom are small, in agreement with the expectations of other investigators that changes in the diamagnetic terms are relatively unimportant in atoms having 2p valence electrons.[4] We further note that the one-center term Q_{AB} contributes to a greater degree than the two-center terms ΣQ_{AB}. Values of the chemical shift, δ^{calcd}, also shown in Table I, are in good agreement with experiment, at least giving the correct order within each molecule. The effect of C as a nearest neighbor is clearly brought out by this method, but the secondary differentiation due to nonneighbor C effects is less accurately reproduced, especially in the underestimation of the 7.2-ppm gap between B-8 and B-9 in o-carborane. The two points at the upper left of the graph (Figure 1) correspond to ^{11}B having two C neighbors, the group of four in the center to one neighbor, and the three at the right to no neighbors.

Thus, the boron chemical shifts in the icosahedral carboranes can be satisfactorily explained on the basis of a difference primarily in the paramagnetic shielding of boron atoms in different chemical environments. Finally, we expect that these local paramagnetic effects

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[2] (a) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838, 1846 (1961); (b) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722, 731 (1961); (c) J. A. Pople, *Mol. Phys.*, 7, 301 (1963–1964); (d) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

[3] J. E. Kent and E. L. Wagner, *ibid.*, **44**, 3530 (1966).

[4] (a) M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1961); (b) R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *ibid.*, **38**, 380 (1963); (c) F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963); (d) C. D. Cornwell, *ibid.*, **44**, 874 (1966).

[5] (a) D. R. Armstrong and P. G. Perkins, *Chem. Commun.*, 337 (1965); (b) C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962).

[6] H. C. Beachell and D. W. Beistel, *Inorg. Chem.*, **3**, 1028 (1964).

[7] (a) G. D. Vickers, A. Agahigian, E. A. Pier, and H. Schroeder, *ibid.*, **5**, 693 (1966); (b) J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Am. Chem. Soc.*, **88**, 628 (1966).

[8] F. P. Boer, J. A. Potenza, and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1301 (1966).

[9] (a) R. M. Stevens and W. N. Lipscomb, *J. Chem. Phys.*, **42**, 3666 (1965); (b) R. Hegstrom and W. N. Lipscomb, *ibid.*, in press

[10] (a) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2361 (1966); (b) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2353 (1966).

[11] W. E. Palke and W. N. Lipscomb, *ibid.*, **88**, 2384 (1966).

[12] Although these matrix elements can have appreciable magnitudes, it was hypothesized[10b] that their omission in the present method might lead to more accurate charge distributions for larger boron frameworks. Analysis of the wavefunction of tetrahedral B_4H_4, the only higher boron hydride which has been studied by SCF methods (W. E. Palke and W. N. Lipscomb, to be published), supports this hypothesis.

Table I

Isomer	Atom	Q_{AA}	ΣQ_{AB}	$\sigma^{(d)}$	δ Obsd[a]	δ Calcd[b]
o (1,2)	B3	1.211	0.123	187.8	15.2	16.7
	B4	1.250	0.128	188.8	13.9	12.5
	B8	1.300	0.131	190.0	9.9	7.4
	B9	1.300	0.136	190.0	2.7	6.8
m (1,7)	B2	1.197	0.123	187.6	17.3	18.2
	B4	1.251	0.127	188.8	13.6	12.5
	B5	1.252	0.131	188.8	11.0	11.9
	B9	1.301	0.132	190.0	7.0	7.2
p (1,12)	B2	1.251	0.127	188.8	15.2	12.5

[a] See ref 7. The chemical shifts are expressed in parts per million from boron trifluoride etherate. [b] These values are calculated using the equation of the least-squares line given in Figure 1: $\delta^{\text{calcd}} = \sigma^{(d)} - 12.4 - 118.9(Q_{AA} + \Sigma Q_{AB})$.

will probably dominate the chemical shifts of other boron compounds.

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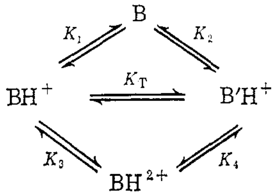
Excited State p*K*'s. IV. Tautomeric Equilibria

Sir:

It has been shown[1] that the equilibrium constants for acid-base reactions in electronically excited states can be obtained, if only approximately, from the electronic absorption spectra of the conjugate acid-base pair by use of the Förster cycle. In principle, the method should be applicable to any type of equilibrium constants. Of particular interest may be tautomeric equilibria which, when occurring in polar media, may be expressed as a combination of several acid-base reactions, and which may be established fast enough to occur in excited singlet states. In connection with our studies of the basic properties of amino-substituted azo and azoxy compounds,[2] we have observed some rather extreme cases of shifts of tautomeric equilibria between ground and excited states.

If we examine the equilibrium diagram for the possible equilibria in the first two protonations of a dibasic acid, we arrive at the following scheme in which BH^+ and $B'H^+$ are two tautomeric first conjugate acids of the base B which differ only in the position of attachment of the proton.[3] The equilibrium between BH^+ and $B'H^+$ is defined by the equilibrium constant $K_T = [BH^+]/[B'H^+] = K_2/K_1 = K_3/K_4$.



We have recently observed a number of such equilibria in which the equilibrium constants undergo tremendous changes upon excitation. Thus, the equilibrium between the azonium and ammonium forms of dimethylaminoazobenzene (DMAB) first conjugate acid, in which both forms are present in measurable quantities ($K_T = 7.15$), shifts, upon excitation, in the direction of the pure azonium form to the complete exclusion of the ammonium form ($K_T^* \approx 10^{26}$). Similarly, in the first conjugate acid of the N-oxide of DMAB, the equilibrium shifts from a pure N-hydroxy-DMAB cation ($K_T \approx 10^6$) in the ground state to a pure azonium cation ($K_T^* \approx 10^{-9}$) in the singlet excited state. In dimethylaminoazoxybenzene a similar change from an ammonium to an azonium form occurs ($K_T \approx 10^8$; $K_T^* \approx 10^{-21}$). In the amino N-oxide of the latter compound, the change in K_T is still quite large, but the equilibrium position is not reversed; the N-hydroxyammonium salt is stable in ground and excited states. However K_T^* is quite small, and it seems feasible that the hydroxyazonium form may be observable. Finally, a similar analysis of the aminonaphthols[4] suggests that K_T changes are much smaller, and no reversal of stable forms occurs; *i.e.*, the neutral form rather than the zwitterion is the stable form in both ground and excited states.

Table I

Compd	pK_1	pK_1*	pK_2	pK_2*	pK_3	pK_3*	pK_4	pK_4*	pK_T	pK_T*
p-Dimethylaminoazobenzene	4.42[a]	−9.64[e]	5.27[f]	7.84[e]	−4.43[h]	10.76[e]	−5.28[f]	−15.59[e]	−0.85[h]	−26.3[e]
p-Dimethylaminoazobenzene N-oxide	−4.91[b]	9.84[f]	4.11[g]	4.11[e]	4.37[f]	4.37[e]	−4.65[g]	10.1[e]	−9.02[f]	5.7[f]
β-Dimethylaminoazoxybenzene	−5[c]	5.6[f]	2.62[g]	−15.58[e]	−0.4[f]	−18.5[j]	−8.02[g]	2.68[e]	−7.6[f]	20[f]
β-Dimethylaminoazoxybenzene N-oxide	−8.59[d]	1.22[f]	3.71[g]	3.71[e]	3.89[f]	3.89[k]	−8.41[g]	1.39[e]	−12[f]	−2[f]
2,3-Aminonaphthol	11.2[a]	6.7[a]	6.0[f]	0.3[e]	2.8[i]	−8.2[e]	8.0[c]	−1.8[a]	5.2[f]	6.4[f]

[a] Calculated from the Hammett equation using parameters from H. H. Jaffé, *Chem. Rev.*, **53,** 191 (1953). [b] Presumed equal to the p*K* of *p*-phenylazo-N,N,N-trimethylanilinium ion.[2a] [c] Calculated from the Hammett equation using parameters from ref 2c. [d] Calculated from the Hammett equation assuming $\sigma_{NO(CH_3)_2} = \sigma_{N(CH_3)_3}$. [e] Calculated from the Förster cycle. [f] Calculated from the relationships within the equation scheme. [g] Experimental, Ellerhorst and Jaffé, unpublished work. [h] Experimental.[2a] [i] Experimental.[4] [j] Constant Δp*K* assumed for equilibria 2 and 3. [k] Assumed Δp*K* = 0.

The data here presented are subject to a great deal of uncertainty. First, the Förster cycle is used throughout, and is known to yield only approximate results.[1b,5]

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[1] *Cf.*, *e.g.* (a) H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *J. Am. Chem. Soc.*, **86**, 2932 (1964); (b) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

[2] (a) S. J. Yeh and H. H. Jaffé, *J. Am. Chem. Soc.*, **81**, 3283 (1959); (b) M. Isaks and H. H. Jaffé, *ibid.*, **86**, 2209 (1964); (c) C. S. Hahn and H. H. Jaffé, *ibid.*, **84**, 949 (1962).

[3] Note that throughout basicities of bases are expressed as pK_a of the conjugate acid.

[4] D. W. Ellis and L. B. Rogers, *Spectrochim. Acta*, **20**, 1709 (1964).

[5] (a) E. L. Wehry and L. B. Rogers, *ibid.*, **21**, 1976 (1965); (b) J. C. Haycook, S. F. Mason, and B. E. Smith, *J. Chem. Soc.*, 4897 (1963).