the potassium ion may be expected to approach aniline approximately along the dipole axis, it is evident that the π cloud of the aromatic ring would come quite close to the ion and a particularly favorable induced dipole and dispersion interaction should result. This effect would further explain the large potassium ion affinity observed for aniline.

References and Notes

(1) Based on Ph.D. Thesis of W. R. Davidson.

(2) (a) A. M. Hogg and P. Kebarle, *J. Chem. Phys.*, **43**, 449 (1965); (b) P. Kebarle, "Ions and Ion Pairs in Organic Reactions", Vol. 1, M. Szwarc, Ed., Wiley, New York, N.Y., 1972.

(3) P. Kebarle, "Modern Aspects of Electrochemistry", Vol. 9, B. E. Conway and J. O'M. Bockris, Ed., Plenum Press, New York, N.Y., 1974.

(4) I. Dzidic and P. Kebarle, *J. Phys. Chem.*, **74**, 1975 (1970).

(5) W. R. Davidson and P. Kebarle, *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) S. K. Searles and P. Kebarle, *Can. J. Chem.*, **47**, 2620 (1961).

(7) W. R. Davidson, Ph.D. Thesis, Chemistry Department, University of Alberta, 1975.

(8) R. J. W. Le Fevre and P. Russel, *Trans. Faraday Soc.*, **63**, 374 (1967).

(9) A. Almenningen and O. Bastiansen, *Acta Chem. Scand.*, **9**, 815 (1955).

(10) K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, **97**, 4179 (1975).

(11) W. R. Davidson and P. Kebarle, *Can. J. Chem.*, submitted for publication.

(12) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504 (1973).

(13) P. Kebarle, R. Yamdagni, K. Hiraoka, and T. B. McMahon, *J. Mass Spectrom. Ion Phys.*, **19**, 71 (1976).

(14) H. C. Brown, *J. Chem. Soc.*, 1248 (1956), and references therein.

(15) (a) G. H. F. Diercksen and W. P. Kraemer, *Theor. Chim. Acta*, **23**, 387 (1972); (b) E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 1077 (1972); H. Kisenmacher, H. Popkie, and E. Clementi, *ibid.*, **58**, 1689 (1973); **59**, 5892 (1973).

(16) A. Hinchliffe and J. C. Dobson, *Theor. Chim. Acta*, **39**, 17 (1975).

(17) K. Spears, *J. Chem. Phys.*, **57**, 1850, 1884 (1972).

(18) I. Eliezer and Q. Krindel, *J. Chem. Phys.*, **57**, 1884 (1972).

(19) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970).

(20) T. Nishikawa, T. Itoh, and K. Shimoda, *J. Chem. Phys.*, **23**, 1735 (1955); V. Shomaker, *Acta Crystallogr.*, **3**, 46 (1950).

(21) A. L. McLennan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.

(22) The Mulliken populations tend to overemphasize centers with larger basis functions, thus, for example, the calculated Mulliken electron populations on hydrogen generally are lower than they should be.

(23) The atomic polarizabilities $\alpha_N = 0.98$, $\alpha_C = 1$, and $\alpha_H = 0.44$ Å^3 were used for ammonia and the methylamines. These values were obtained from the molecular polarizabilities of the above compounds (determined by Le Fevre[8]) by assuming that the molecular polarizabilities can be expressed as a sum of the polarizabilities α_N, α_C, and α_H of the constituent atoms.

(24) J. S. Muirhead-Gould and K. J. Laidler, *Trans. Faraday Soc.*, **63**, 944 (1967).

(25) K. S. Pitzer, *Adv. Chem. Phys.*, **2**, 59 (1952).

(26) I. Amdur, J. E. Jordan, L. W. M. Fung, L. J. F. Hermans, S. E. Johnson, and R. L. Hance, *J. Chem. Phys.*, **59**, 5329 (1973).

(27) Strictly speaking the E_t are not directly comparable with $\Delta H_{0,1}$. The difference between the two values is largely composed of the zero-point energies for the three new vibrations in the ion–molecule complex. These amount to about 2 kcal/mol[18] such that $E_t + 2 \approx \Delta H_{0,1}$. Since the purpose of the present calculations is to obtain qualitative insights this small difference is not taken into consideration.

(28) R. L. Woddin and J. L. Beauchamp, unpublished results.

(29) The geometry for the methylamine series $NH_3 \cdots (CH_3)_3N$ was not optimized in the electrostatic calculation. The axis between the K^+ and the N atom was assumed to pass symmetrically through the NH_3 molecule. The methyl groups were then introduced by replacing H with CH_3 without changing the angle of the NH_3 molecule to the N–K^+ axis. Thus, the calculations for CH_3NH_2 and $(CH_3)_2NH$ which have *no* threefold symmetry axis are somewhat in error. The geometry optimized binding energies for these two molecules are expected to be somewhat larger.

(30) It should not be forgotten that the changes of the experimental $\Delta H_{0,1}$ with methyl substitution particularly between dimethylamine and trimethylamine are essentially within experimental error. Therefore a small lowering rather than a small increase of the $-\Delta H_{0,1}$ cannot be excluded on the basis of the present experiments. Considering the assumption made in the electrostatic calculations a similar error could exist there also. Therefore the important point is that because of the operation of the mentioned opposing factors the increases are very small, so small that they might even reverse for the last pair.

(31) M. J. Aroney, R. J. W. Le Fevre, L. Radom, and C. D. L. Ritchie, *J. Chem. Soc. B*, 507 (1968).

MCD Spectra of Diphenylmethyl Cation and Anion. A Test of the Pairing Theorem[1]

Karl L. Tseng and Josef Michl*

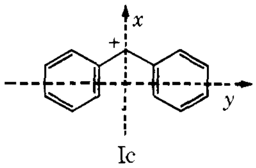
Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

Received February 19, 1976

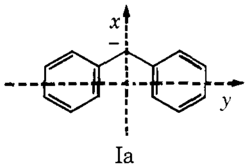
Abstract: Magnetic circular dichroic spectra of the $(C_6H_5)_2CH^+$ and $(C_6H_5)_2CH^-$ ions are approximate mirror images of each other as predicted by the pairing theorem within the framework of the π-electron Pariser-Parr-Pople (PPP) model. The spectra reveal the existence of two transitions in what appears to be the first absorption band in each ion. The observed absolute MCD signs are in agreement with results of PPP calculations and also with simple arguments based on inspection of Hückel orbitals of the ions.

A general theorem[2] valid for the Pariser-Parr-Pople (PPP) model[3] states that π-electron contributions to the magnetic circular dichroic (MCD) spectra of two species paired in the sense of alternant symmetry[4] should be mirror images of each other (their absorption spectra should be identical[4,5]). Since this a priori prediction follows from the fundamental structure of the PPP model and is independent of the choice of parameters and most other calculational details, an experimental test will provide important indications of the extent to which the model is valid for π electrons and of the role which σ electrons play in codetermining the MCD spectra of π chromophores. This is of particular interest in view of the recent questioning of the validity of the concept of alternant symmetry and pairing based on ab initio calculations on benzene.[6]

It is known[7] that the differences of experimental absorption spectra of the members of a cation-anion pair are small for ions with well delocalized charge, such as radical ions of even alternant hydrocarbons, and somewhat larger for ions with charge largely localized at one atomic center, such as polyarylmethyl ions. This has been tentatively attributed to the larger sensitivity of anions of the latter kind to effects of pairing with the counterion but could also be due to deficiencies in the PPP model. We have selected the diphenylmethyl ions (Ic, Ia) as a fairly demanding case for testing the PPP prediction and used solvents believed to minimize ion association. Ions Ic and Ia are well known,[7-9] and their



Ic



Ia

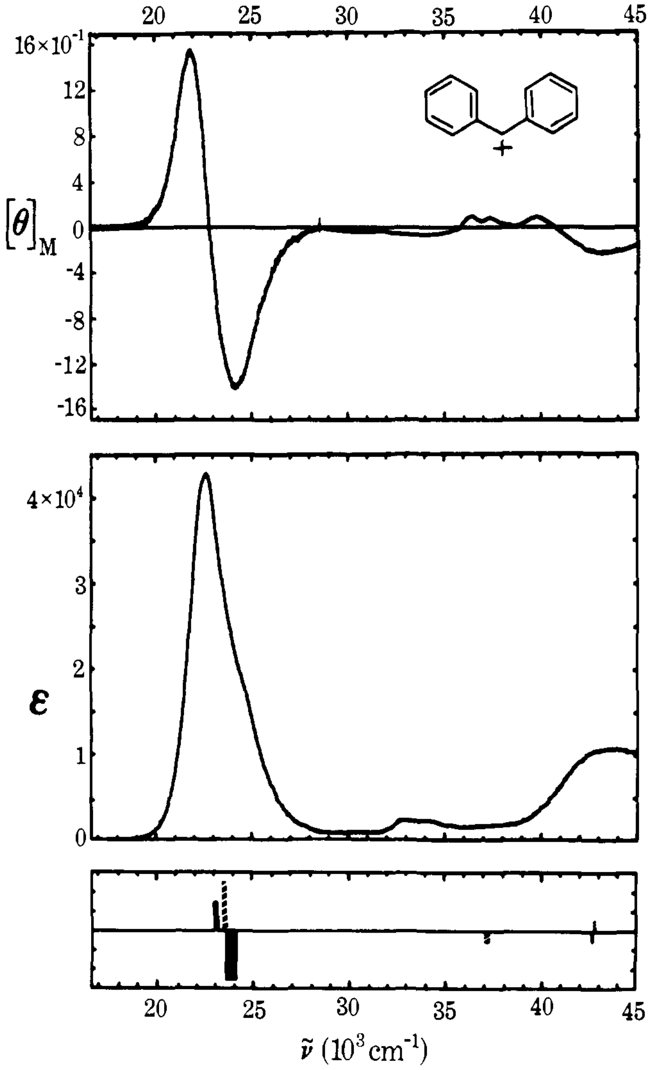


Figure 1. Diphenylmethyl cation (Ic) in H_2SO_4. Top: MCD; center: absorption; bottom: PPP calculation (thick lines: oscillator strength above 0.2; thin lines: below 0.02; dashed lines: short-axis polarized; full lines: long-axis polarized; long lines: the absolute magnitude of B term above 10^{-2} D^2 β_e/cm^{-1}; short lines: below 10^{-3} D^2 β_e/cm^{-1}; upper part: positive MCD; lower part: negative MCD).

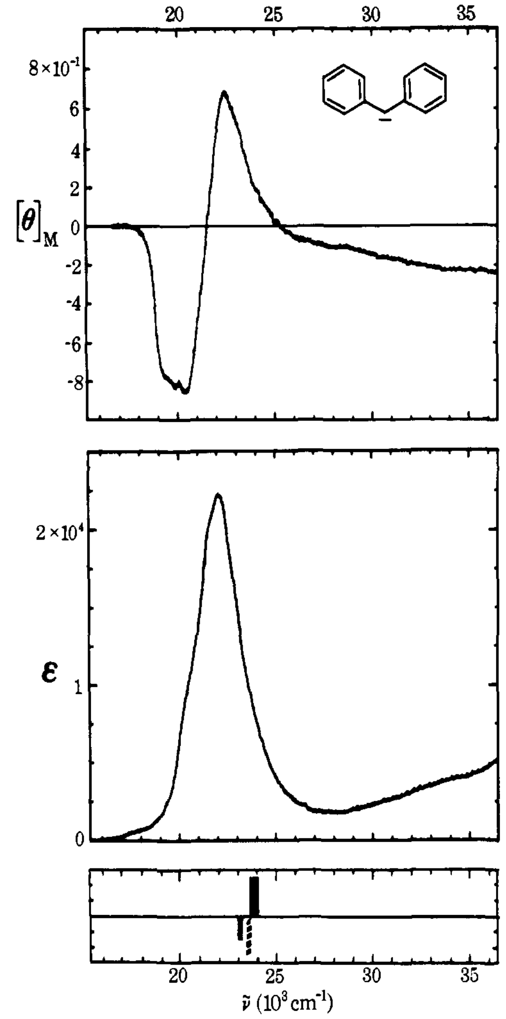


Figure 2. Diphenylmethyl anion (Ia) in hexamethylphosphoramide. See caption to Figure 1.

electronic absorption spectra have been rationalized in terms of simple Hückel theory.[5,7,10] The Hückel model predicts accidental threefold degeneracy for the lowest excited state.[7] More elaborate calculations have also been reported, using the simple PPP method[9] and a variable electronegativity version thereof,[11] for which the exact pairing property is no longer present, so that some differences are predicted between the spectra of Ic and Ia. In these PPP calculations, the threefold degeneracy is slightly split. Experimentally, no convincing evidence has been available for the presence of more than one electronic transition in the strong band observed near 430 nm.[7-9]

In the present paper, we report a measurement and PPP calculation of MCD spectra for Ic and Ia and find good agreement with expectations based on the mirror-image theorem.[2] Simultaneously with our initial report[1] of these results, a communication[12] on MCD spectra of two additional pairs has appeared. These were the radical cation-radical anion and double cation-double anion of perylene. Also for these two pairs, the expected mirror image relation was confirmed.[12]

Experimental Section

Sample Solutions. Diphenylmethanol was prepared by $LiAlH_4$ reduction of benzophenone (Matheson Coleman and Bell), crystallization, and gradient sublimation. Solutions containing Ic were prepared by dissolving the carbinol in spectral grade concentrated H_2SO_4 or distilled $HFSO_3$ (under N_2). Measurements were performed on freshly prepared solutions.

Diphenylmethane (Matheson Coleman and Bell) was purified by vacuum distillation, hexamethylphosphoramide (HMPA, Aldrich) was vacuum distilled over CaH_2, and NaH (Baker) was washed several times with absolute ether. Standard vacuum line (10^{-6} Torr) procedures (potassium mirror getter) were used for the preparation of Ia by reaction of diphenylmethane with NaH in HMPA in a sealed all-Pyrex vessel with an attached quartz optical cell. The reaction was complete after 3 weeks.

Spectroscopy. Absorption spectra were recorded on a Cary 17 spectrophotometer; MCD instrumentation has been described elsewhere.[13] Optical paths of Suprasil cells were 0.5 and 1 mm for Ia and 1 cm for Ic. The same spectra for Ic were obtained in H_2SO_4 and $HFSO_3$. Absorption spectra agreed with those reported (there is considerable scatter in the extinction coefficients reported for Ic). Oscillator strengths were evaluated as $f = 4.319 \times 10^{-9} \int \epsilon \, d\tilde{\nu}$ and B terms as $B = -(33.53\tilde{\nu}_0)^{-1} \int [\theta]_M \, d\tilde{\nu}$, where $\tilde{\nu}_0$ is the band center in cm^{-1} and $[\theta]_M$ is molar ellipticity per unit field in deg l. mol^{-1} m^{-1} G^{-1}.

Calculations. PPP SCF-CI calculations were performed as described in ref 14, using all singly excited configurations and standard parameters [$\beta = -2.318$ eV, $\gamma_{\mu\nu} = 14.399/(1.328 + r_{\mu\nu})$].

Results and Discussion

The absorption and MCD spectra of Ic and Ia are shown in Figures 1 and 2, respectively. Table I compares the spectral observables with results of our PPP calculations. It appears very likely that Ic in H_2SO_4 and Ia in HMPA exist ei-

Table I. Spectral Data for Ic and Ia

			Transition No.								
			1	2	3	4	5	6	7	8	9
PPP	I	E^a	23.05	23.52	23.86	37.10	42.65	42.76	45.40	48.57	51.66
SCI		$f_r{}^b$	0.04	0.06	0.94	0.11	0.002	0.0002	0.05	0.0002	0.68
		$f_p{}^b$	0.04	0.006	0.52	0.04	0.002	0.0002	0.04	0.0002	0.32
		Pol[c]	*y*	*x*	*y*	*x*	*y*	*x*	*y*	*x*	*y*
	Ic	$B_t{}^d$	−2.65	−49.45	+51.69	+0.24	+0.05	−0.07	+0.23	−0.01	+0.18
		$B_b{}^d$	−2.53	−50.85	+53.11	+0.32	+0.05	−0.07	−0.05	−0.01	+1.00
	Ia	*B* Same as Ic except with opposite signs									
Exp	Ic	E^a		21.9	24.3						
		f^e		0.8							
		B^f		−4.9	+6.1						
	Ia	E^a		19.2–20.3	22.5						
		f^e		0.5							
		B^f		+4.3	−2.4						

[a] Transition energy in 10^3 cm^{-1}. [b] Oscillator strength: f_r from dipole length formula, f_p from dipole velocity formula. [c] Polarization: *y*, long axis; *x*, short axis. [d] Calculated *B* terms in units of 10^{-3} D^2 β_e/cm^{-1}. The values given indicate the extremes of the range covered by the calculated *B* term when the origin moves from the top end of the molecule (B_t) to the bottom end (B_b) in formulas Ic and Ia. [e] Experimental oscillator strength. [f] Experimental *B* terms.

ther as free ions or loose ion pairs, but rigorous proof is not available (cf. ref 15).

While the absorption spectra of Ic and Ia are very similar (except that absorption of Ic is stronger), their MCD spectra are very close mirror images of each other (except that the intensities are higher in the case of Ic). This result, particularly when considered together with the similar recent observations[12] for the perylene radical ions and double ions, represents a gratifying confirmation of the a priori theoretical prediction of the PPP model. It indicates that the model correctly incorporates the fundamental features of the electronic structure of π-electron systems and it provides further support for the important concept of state pairing. Moreover, it indicates that consideration of magnetic mixing of ππ* states with excited states involving promotion from or into σ orbitals is not essential for the understanding of the behavior of ππ* transitions in the long-wavelength region in the MCD spectra of π-electron chromophores. This is important since the PPP model is much simpler than all-valence electron models and lends itself readily to the use of pictorial arguments for absolute signs of *B* terms, which require no computations at all,[14,16,17] and to the derivation of general rules, e.g., for effects of substitution on benzene[17,18] and polycyclic hydrocarbons.[1,19] At the same time, it is obvious that the PPP model is not exact, and MCD spectroscopy provides an interesting new method for exploration of the ways in which it deviates from reality.

The MCD spectra provide the first piece of experimental evidence in favor of the composite nature of the 22–23 000 cm^{-1} absorption band in the spectra of Ic and Ia. The MCD spectral shapes are reminiscent of those observed for transitions into doubly degenerate excited states (*A* terms). Since symmetry of Ic and Ia is not sufficiently high to permit degenerate states, the MCD shape must be interpreted as due to accidental near degeneracy in the excited state leading to two *B* terms of opposite signs.

π-Electron calculations assign low-energy transitions in Ic to electron jumps from several of the highest occupied molecular orbitals (HOMO's) into the lowest unoccupied ("nonbonding") orbital (LUMO) and those in Ia to jumps from the ("nonbonding") HOMO to the several lowest LUMO's. As mentioned in the introduction, the simple Hückel model predicts the HOMO of Ic as well as the LUMO of Ia to be triply degenerate. In the PPP model, this is still approximately true. Indeed, the transitions from the three HOMO's into the LUMO in Ic as well as their "mirror image" transitions from the HOMO to the three LUMO's in Ia are calculated to occur at almost the same energy (Table I). Inspection of these orbitals shows that one of the three approximately degenerate transitions should be weak and short-axis polarized (X), whereas two, one weak (Y_1) and the other very strong (Y_2), should be long-axis polarized. Consideration of the effects of configuration interaction has essentially no effect on these conclusions. The much larger intensity of one of the three transitions explains why the absorption curve shows essentially no indication of the presence of weaker transitions buried underneath. In the related triphenylmethyl cation, whose MCD spectra have been measured recently,[15] the situation is even more complicated since fivefold degeneracy is predicted for the lowest excited state at the Hückel level. In the PPP model for propeller-shaped geometry, these states split into $2A_1 + A_2 + E$: the transitions to the two A_1 states are forbidden, transition into A_2 is polarized along the threefold axis, and transition into the degenerate E state is polarized in a plane perpendicular to this axis.[7] The relative intensity of the two allowed transitions depends on the degree of propeller twist. In H_2SO_4 and $HFSO_3$ solvents, the lowest wavelength transition at 430 nm apparently is into the E state since an *A* term appears at this wavelength in the MCD spectrum. The shorter wavelength transition at 406 nm then is into the A_2 state and its negative *B* term is apparently superimposed in the MCD spectrum on the short-wavelength tail of the *A* term, so that only a weak positive MCD peak appears near 380 nm. The reasonable agreement of the MCD spectra in H_2SO_4 and $HFSO_3$ solvents with simple-minded expectations is encouraging for our present attempts to rationalize the MCD spectra of Ic and Ia in these solvents. In other solvents, however, the spectra of the triphenylmethyl cation show some interesting complications presumably due to ion pairing which changes the shape of the propeller.[15]

The PPP prediction of the order of the three transitions in Ia and Ic, Y_1, then X, and then at highest energy Y_2, cannot be considered reliable since the energy differences are miniscule (Table I). Indeed, the published calculation by a modified PPP method[11] gave a different order from ours and also different order in Ic and in Ia. It might thus appear that the agreement of the calculated order of MCD signs with experiment displayed in Table I is purely fortuitous, since the employed formula[20] for *B* involves division by energy differences:

$$B(\mathrm{G} \rightarrow \mathrm{F}) = \mathrm{Im}\left\{\sum_{\mathrm{I}\neq\mathrm{G}} \langle \mathrm{I}|\hat{\boldsymbol{\mathcal{M}}}|\mathrm{G}\rangle \cdot \langle \mathrm{G}|\hat{\mathbf{M}}|\mathrm{F}\rangle \times \langle \mathrm{F}|\hat{\mathbf{M}}|\mathrm{I}\rangle/(W_\mathrm{I} - W_\mathrm{G}) + \sum_{\mathrm{I}\neq\mathrm{F}} \langle \mathrm{F}|\hat{\boldsymbol{\mathcal{M}}}|\mathrm{I}\rangle \cdot \langle \mathrm{G}|\hat{\mathbf{M}}|\mathrm{F}\rangle \times \langle \mathrm{I}|\hat{\mathbf{M}}|\mathrm{G}\rangle/(W_\mathrm{I} - W_\mathrm{F})\right\}$$

Here, G is the ground state, F the final state, $\hat{\mathbf{M}}$ the electric dipole moment operator, $\hat{\boldsymbol{\mathcal{M}}}$ the magnetic dipole moment operator, W_I is the energy of Ith state, and the summations are run over all molecular electronic states I except as shown.

Closer examination reveals, however, that the predicted order of MCD signs is independent of the details of ordering of states X, Y_1, and Y_2, and indeed of all details of the calculation, and can be understood by simple inspection of Hückel MO's without any calculation using techniques of ref 14. This is possible since the three nearly degenerate singly excited configurations mix very little when CI is introduced into the PPP description. As might be suspected at first sight, the calculated B terms of the nearly degenerate transitions X, Y_1, and Y_2 are due to the mutual magnetic mixing of their excited states, and mixing with other states makes totally negligible contributions. The contribution from mutual mixing of excited states of transitions Y_1 and Y_2 vanishes by symmetry, so that only two quantities remain to be considered, due to X-Y_1 and X-Y_2 mixing. Since the transition Y_2 is much stronger than transition Y_1, it is no surprise that the calculated effect of magnetic mixing X-Y_2 dominates not only the sign of the B term of transition Y_2 but also that of transition X. The other mixing, X-Y_1, then only determines the sign of the B term of transition Y_1, whose calculated magnitude is so small so that it is likely to be buried under the strong MCD peaks due to transitions X and Y_2. Experimentally, we find no clear-cut evidence for it in the MCD spectrum. Thus, although the theoretical arguments for the presence of three transitions appear convincing to us, it remains to be proven that three rather than just two are indeed present, and polarization measurements might achieve this.

In order to understand the MCD signs arising from X-Y_2 mixing, we shall concentrate on the case of Ic (the case of Ia is completely analogous). The contribution to the B term of transition X which originates in X-Y_2 mixing can be written as

$$B(\mathrm{X \ from \ Y_2}) = \mathrm{Im}\left\{\frac{\langle \mathrm{X}|\hat{\boldsymbol{\mathcal{M}}}|\mathrm{Y}_2\rangle}{W_{\mathrm{Y}_2} - W_\mathrm{X}} \cdot \langle \mathrm{G}|\hat{\mathbf{M}}|\mathrm{X}\rangle \times \langle \mathrm{Y}_2|\hat{\mathbf{M}}|\mathrm{G}\rangle\right\}$$

Obviously, the contribution to the B term of transition Y from the same mixing will be $B(\mathrm{Y_2 \ from \ X}) = -B(\mathrm{X \ from \ Y_2})$. The sign of the triple product can be evaluated easily by inspection of the MO's involved in the transitions X and Y_2 (the only potential problem is distinguishing which of the three HOMO's is involved in transition Y_1 and which one in transition Y_2, but this is easily accomplished by inspection of the transition dipoles: that for Y_2 is large, that for Y_1 small). We find it easiest to use the three-sign rule described in detail in ref 14. The resulting sign of $B(\mathrm{X \ from \ Y_2})$ depends on the sign of the energy difference $W_{\mathrm{Y}_2} - W_\mathrm{X}$. If X lies at lower energy than Y_2, the sign derived by orbital inspection using methods of ref 14 is $B(\mathrm{X \ from \ Y_2}) < 0$, i.e., the MCD peak of transition X should be positive and that of Y_2 should be negative. This is in agreement with our PPP calculation and with experiment. If X were to lie at higher energy than Y_2, the sign of $W_{\mathrm{Y}_2} - W_\mathrm{X}$ would change while the transition moment vectors would remain the same, so that $B(\mathrm{X \ from \ Y_2}) > 0$; i.e., the MCD peak of transition X should now be negative and that of Y_2 positive. Therefore, regardless of the ordering of the states X and Y_2, the lower energy transition should have a positive MCD sign and the higher energy transition should have a negative MCD sign, as is indeed observed for Ic. This argument shows that assignment of the two observed transitions to X and Y_2, respectively, cannot be done on the basis of our data, so that it is not possible to decide at present whether the ordering shown in Table I or that calculated in ref 11 is correct.

The magnitude of the calculated B terms is much too large, even considering the probably considerable cancellation of the two MCD bands observed. This is most likely due both to the use of dipole length formula in our expression for B, known to yield exaggerated oscillator strengths when used at the SCI level, and to errors in the calculation of the energy difference $W_{\mathrm{Y}_2} - W_\mathrm{X}$. It is actually quite amazing that the magnitude of the experimental B terms is so similar in Ic and Ia considering how sensitive it should be to even very small differences in the separation of the X and Y_2 transitions. Such differences could be the origin of most of the minor deviations from the perfect mirror image relation expected from the simple PPP model.[21]

Acknowledgment. This work was supported by Public Health Service Grant GM 21153. The authors are grateful to Professor H. Eyring (University of Utah) for the kind permission to use his MCD instrument. Helium gas was provided by a departmental grant from the Office of Naval Research.

References and Notes

(1) Presented at the First Chemical Congress of the North American Continent, Mexico City, Mexico, Nov. 30–Dec. 5, 1975.
(2) J. Michl, *J. Chem. Phys.*, **61**, 4270 (1974).
(3) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
(4) A. D. McLachlan, *Mol. Phys.*, **2**, 271 (1959); **4**, 49 (1961); J. Koutecký, *J. Chem. Phys.*, **44**, 3702 (1966); **47**, 1501 (1967).
(5) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68**, 591 (1955).
(6) P. J. Hay and I. Shavitt, *J. Chem. Phys.*, **60**, 2865 (1974).
(7) S. F. Mason, *Q. Rev., Chem. Soc.*, **15**, 287 (1961); R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 264 (1964).
(8) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); E. A. Izrailevich, D. N. Shigorin, I. V. Astaf'ev, and A. I. Shatenshtein, *Dokl. Akad. Nauk SSSR*, **111**, 617 (1956).
(9) J. Koutecký and J. Paldus, *Collect. Czech. Chem. Commun.*, **28**, 1483 (1963); V. Horák, C. Párkányi, J. Pecka, and R. Zahradník, *ibid.*, **32**, 2272 (1967).
(10) R. Zahradník, C. Párkányi, J. Michl, and V. Horák, *Tetrahedron*, **22**, 1341 (1966).
(11) J. Wasilewski, *Acta Phys. Pol. A*, **45**, 143 (1974).
(12) R. J. van der Wal and P. J. Zandstra, *Chem. Phys. Lett.*, **36**, 500 (1975).
(13) D. J. Shieh, S. H. Lin, and H. Eyring, *J. Phys. Chem.*, **77**, 1031 (1973).
(14) S. M. Warnick and J. Michl, *J. Am. Chem. Soc.*, **96**, 6280 (1974).
(15) Y. K. Mo, R. E. Linder, G. Barth, E. Bunnenberg, and C. Djerassi, *J. Am. Chem. Soc.*, **96**, 3309 (1974).
(16) J. Kolc, E. W. Thulstrup, and J. Michl, *J. Am. Chem. Soc.*, **96**, 7188 (1974); E. W. Thulstrup, J. Michl, and C. Jutz, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1618 (1975); E. W. Thulstrup and J. Michl, *J. Mol. Spectrosc.*, **61**, 203 (1976); J. Michl, *J. Am. Chem. Soc.*, **98**, 4546 (1976).
(17) J. Michl and J. Michl, *J. Am. Chem. Soc.*, **96**, 7887 (1974); J. Michl, *Chem. Phys. Lett.*, in press.
(18) L. Seamans, Ph.D. Dissertation, University of Minnesota, 1971; L. Seamans and J. Linderberg, *Mol. Phys.*, **24**, 1393 (1972); D. W. Miles and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3754 (1973); A. Kaito, A. Tajiri, and M. Hatano, *J. Am. Chem. Soc.*, **98**, 384 (1976).
(19) J. Michl, *Chem. Phys. Lett.*, **39**, 386 (1976).
(20) P. J. Stephens, *J. Chem. Phys.*, **52**, 3489 (1970).
(21) Note Added in Proof. Additonal experimental evidence for the validity of the mirror image pairing theorem has appeared recently: R. J. van der Wal and P. J. Zandstra, *J. Chem. Phys.*, **64**, 2261 (1976); R. E. Koning and P. J. Zandstra, *Ber. Bunsenges. Phys. Chem.*, **80**, 199 (1976).