(*E*)-*m*-Nitrostyryl vinyl sulfone (4n): mp 117–118 °C (from ethanol); IR (KBr) 1130, 1305, 1365, and 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.9–7.3 (5 H, m) and 7.4–8.5 (4 H, m); MS, *m/z* 239 (M^+); HRMS, *m/z* 239.0256 ($C_{10}H_9O_4NS$ requires 239.0252).

(*E*,*E*)-1-Phenyl-4-(*p*-tolyl)-1,3-butadiene (5a): mp 152–153 °C (lit.[22] mp 155–156 °C), IR (KBr) 3030, 2920, 995, 805, 750, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (3 H, s), 6.3–6.8 (4 H, m), and 6.9–7.6 (9 H, m); MS, *m/z* 220 (M^+).

(*E*,*E*)-1,4-Diphenyl-1,3-butadiene (5b): mp 148–149 °C (from ethanol, lit.[23] mp 149.7 °C); IR (KBr) 3010, 1490, 1440, 990, 740, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.1–6.8 (4 H, m) and 6.9–7.4 (10 H, m); MS, *m/z* 206 (M^+).

(*E*,*E*)-1-(*p*-Chlorophenyl)-4-phenyl-1,3-butadiene (5c): mp 161–162 °C (from ethanol, lit.[22] mp 161 °C); IR (KBr) 3010, 1480, 1090, 980, 840, 745, and 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.6–6.9 (4 H, m) and 7.0–7.6 (9 H, m); MS, *m/z* 240 and 242 (M^+).

(*E*,*E*)-1-(*m*-Nitrophenyl)-4-phenyl-1,3-butadiene (5d): mp 142–143 °C (from ethanol; lit.[24] mp 146 °C); IR (KBr) 3020, 1535, 1350, 990, 755, 735, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.5–6.9 (4 H, m) and 7.0–8.4 (9 H, m); MS, *m/z* 251 (M^+).

(*E*,*E*)-1-(*p*-Chlorophenyl)-4-(*p*-methylphenyl)-1,3-butadiene (5e): mp 206–207 °C (from benzene); IR (KBr) 3020, 1490, 995, 990, 850, and 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (3 H, s), 6.3–6.8 (4 H, m), and 6.9–7.6 (8 H, m); MS, *m/z* 254 and 256 (M^+). Anal. Calcd for $C_{17}H_{15}Cl$: C, 80.15; H, 5.94. Found: C, 80.12; H, 5.91.

(*E*,*E*)-1,4-Bis(*p*-chlorophenyl)-1,3-butadiene (5f): mp 201–202 °C (from benzene); IR (KBr) 3020, 1490, 1400, 1095, 1000, 855, and 800 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.0–6.8 (2 H, m) and 6.9–7.5 (10 H, m); MS, *m/z* 274, 276, and 278 (M^+). Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40. Found: C, 69.80; H, 4.38.

(*E*)-4-Chloro-1-phenyl-1-octene (12a): IR (neat) 3025, 2925, 2860, 1595, 1490, 1450, 965, 745, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.0 (9 H, m), 2.2–2.7 (2 H, m), 3.3–3.9 (1 H, m), and 6.0–7.5 (7 H, m); MS, *m/z* 222 and 224 (M^+); HRMS, *m/z* 222.1157 ($C_{14}H_{19}Cl$ requires 222.1175).

(*E*)-4-Chloro-1-phenyl-1-nonene (12b): IR (neat) 3025, 2950, 2925, 2850, 1595, 1490, 1450, 965, 790, 760, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–2.0 (11 H, m), 2.3–2.7 (2 H, m), 3.3–4.0 (1 H, m), and 5.9–7.4 (7 H, m); MS, *m/z* 236 and 238 (M^+): HRMS, *m/z* 236.1325 ($C_{15}H_{21}Cl$ requires 236.1332).

(*E*)-4-Chloro-1-phenyl-1-decene (12c): IR (neat) 3020, 2940, 2920, 2850, 1490, 1450, 1375, 960, 740, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–2.0 (13 H, m), 2.4–2.7 (2 H, m), 3.6–4.2 (1 H, m), and 6.2–7.4 (7 H, m); MS, *m/z* 250 and 252 (M^+); HRMS, *m/z* 250.1420 ($C_{16}H_{23}Cl$ requires 250.1488).

(*E*)-4-Chloro-4-cyclohexyl-1-phenyl-1-butene (12d): IR (neat) 3060, 3040, 2920, 2850, 1593, 1490, 1445, 960, 740, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.1 (11 H, m), 2.3–2.8 (2 H, m), 3.5–4.1 (1 H, m), and 6.1–7.5 (7 H, m); MS, *m/z* 248 and 250 (M^+); HRMS, *m/z* 248.1283 ($C_{16}H_{21}Cl$ requires 248.1332).

Registry No. **2a**, 52147-97-4; **2e**, 98821-28-4; **2f**, 52147-98-5; **2g**, 98821-29-5; **2l**, 6608-47-5; **3a**, 98821-15-9; **3b**, 68667-91-4; **3c**, 98821-16-0; **3d**, 98821-17-1; **3e**, 98821-18-2; **3f**, 98821-19-3; **3g**, 98821-20-6; **3h**, 98821-21-7; **3i**, 98821-22-8; **3j**, 98821-23-9; **3k**, 98821-24-0; **3l**, 98821-25-1; **3m**, 98821-26-2; **3n**, 98821-27-3; **4a**, 98821-30-8; **4b**, 65350-60-9; **4c**, 98821-31-9; **4d**, 98821-32-0; **4g**, 98821-33-1; **4h**, 98821-34-2; **4i**, 98821-35-3; **4j**, 98821-36-4; **4k**, 98821-37-5; **4l**, 98821-38-6; **4m**, 98821-39-7; **4n**, 98821-40-0; **5a**, 37985-11-8; **5b**, 538-81-8; **5c**, 37985-13-0; **5d**, 57668-32-3; **5e**, 98821-41-1; **5f**, 88539-06-4; **12a**, 98821-42-2; **12b**, 98821-43-3; **12c**, 98821-44-4; **12d**, 98821-45-5; *p*-$CH_3C_6H_4CH{=}CH_2$, 622-97-9; $C_6H_5CH{=}CH_2$, 100-42-5; *p*-$ClC_6H_4CH{=}CH_2$, 1073-67-2; *m*-$NO_2C_6H_4CH{=}CH_2$, 586-39-0; $CH_3(CH_2)_3CH{=}CH_2$, 592-41-6; $CH_3(CH_2)_4CH{=}CH_2$, 592-76-7; $CH_3(CH_2)_5CH{=}CH_2$, 111-66-0; *c*-$C_6H_{11}CH{=}CH_2$, 695-12-5.

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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 27.[1] Mesoionic Compounds

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Magnetic circular dichroism of a series of mesoionic heterocycles derived from a $(4n + 2)$-electron perimeter has been measured and calculated. The spectra permit an identification of L_1 and L_2 bands. The observed MCD signs agree with simple qualitative arguments based on the perimeter model.

Absolute signs of low-energy $\pi\pi^*$ transitions in the magnetic circular dichroism (MCD) spectra of cyclic π-electron systems formally derived from $(4n + 2)$-electron perimeters are frequently very sensitive to the details of molecular structure, such as the nature and position of substituents and heteroatoms. These signs are usually readily predictable from the knowledge of the perturbations which convert the parent $(4n + 2)$-electron perimeter into the molecule in question.[2] The predictions can be semiquantitative, based on explicit MO calculations, typically of the PPP or INDO/S variety, or qualitative, based on the perimeter model, which requires only the knowledge of the relative size of the gaps between the two highest occupied molecular orbitals (ΔHOMO) and between the two lowest unoccupied MO's (ΔLUMO) derived from the perimeter. The relative size may be obvious by inspection, using the PMO theory. In particularly complicated cases, it may have to be obtained from a calculation. The simplicity of the perimeter model is appealing not only for facile predictions of MCD signs but also for providing physical insight into the origin of the signs obtained using computer programs. Perhaps equally important is its contribution to the organization of knowledge concerning UV and MCD spectra of large classes of compounds which may appear widely dissimilar at first sight.

Since the perimeter model is based on perturbation theory, it is interesting to ask how strong a perturbation is needed before the model fails to account for the observed MCD signs. From this point of view, mesoionic compounds[3] represent a challenging test case. The electronic

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0022-3263/85/1950-5050$01.50/0

structure of these compounds is nonclassical in that they have to be written as hybrids of several charge-separated or long-bond valence-bond formulas. Although compounds such as **1A**, **2A**, and **3** (Chart I) clearly contain an array of parallel 2p orbitals with cyclic π overlap, like their respective parent 6π-electron perimeters $C_5H_5^-$, C_6H_6, and $C_{10}H_{10}$, the series of strong perturbations needed for their formal derivation from a perimeter, **1a** → **1b** → **1c** → **1d** → **1A**, **2a** → **2b** → **2c** → **2A**, **3a** → **3b** → **3c** → **3d** → **3e** → **3**, is such that an extensive debate has been underway for some time as to whether it is useful to classify sydnones and other $(4n + 2)\pi$-electron cyclic mesoionic compounds as aromatic at all.[4-6] Certainly, the distribution of electronic density and bond orders in the ground state of **1** is far less even than in $C_5H_5^-$, and although this may be less so in the various $\pi\pi^*$ excited states of the system, there is a strong temptation to describe its ground-state electronic structure in terms of only weakly interacting subunits.

We shall see in the following that even these distant relatives of the parent $(4n + 2)$-electron perimeters obey the simple rules for MCD signs of a perturbed perimeter. This is quite remarkable and is undoubtedly due to the circumstance that nodal properties of the perimeter MO's, which are ultimately responsible for the MCD signs, are almost impossible to change substantially, even by the strongest of perturbations. On the other hand, we have found that the standard semiempirical methods, PPP and INDO/S, do rather poorly in accounting for the UV and MCD spectra.

UV spectra of alkylsydnones are characterized by an intense (log $\epsilon \sim 4$) absorption band near 34 000 cm^{-1} (290 nm).[7] This band exhibits a negative solvatochromic effect[8] (increased solvent polarity induces a hypsochromic shift) and has been assigned to a $\pi\pi^*$ transition.[9] UV spectra of 4,6-dioxo-1,3-diazines show bands near 29 000 cm^{-1} (350 nm; log $\epsilon \sim 3$) and 38 000 cm^{-1} (260 nm; log $\epsilon \sim 4$).[3] MCD spectra of mesoionic compounds do not appear to have been investigated prior to this work.

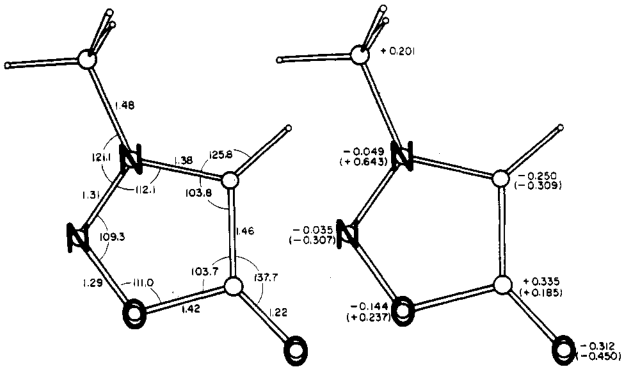

Figure 1. **1A**: MNDO bond lengths (Å) and angles (deg) and net atomic charges (π charges in parentheses).

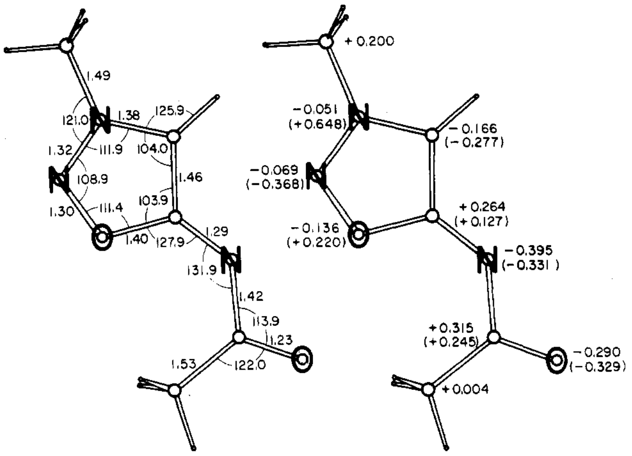

Figure 2. **1C**: MNDO bond lengths (Å) and angles (deg) and net atomic charges (π charges in parentheses).

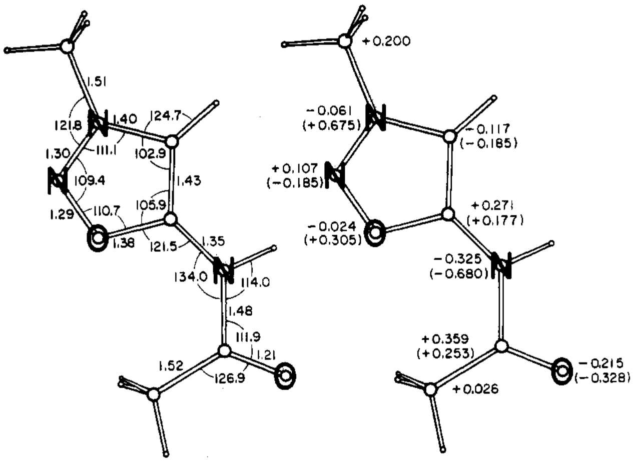

Figure 3. **1D**: MNDO bond lengths (Å) and angles (deg) and net atomic charges (π charges in parentheses).

Experimental Section

Samples. Published synthetic procedures (**1A**,[10] **1B**,[11] **1C**,[12] **2A**,[13] **2B**,[13] **3**[14]) were followed by crystallization from suitable solvents. Solutions were prepared in spectral grade acetonitrile, stored over molecular sieve 3A under argon. A solution of the hydrochloride **1D** was prepared by dissolving **1C** in dilute hydrochloric acid.[12]

Measurements. Absorption spectra were taken on a Cary 17 spectrometer, MCD spectra on a JASCO J-500C dichrograph equipped with a JASCO electromagnet (1.504 T). Both instru-

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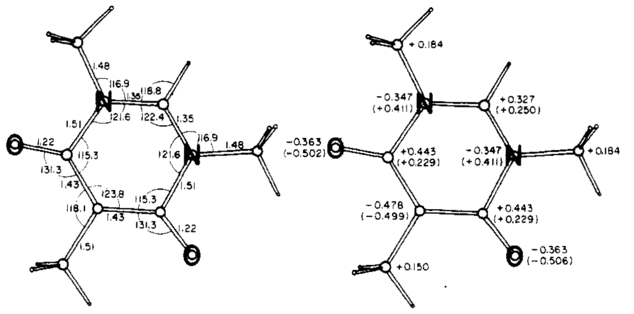
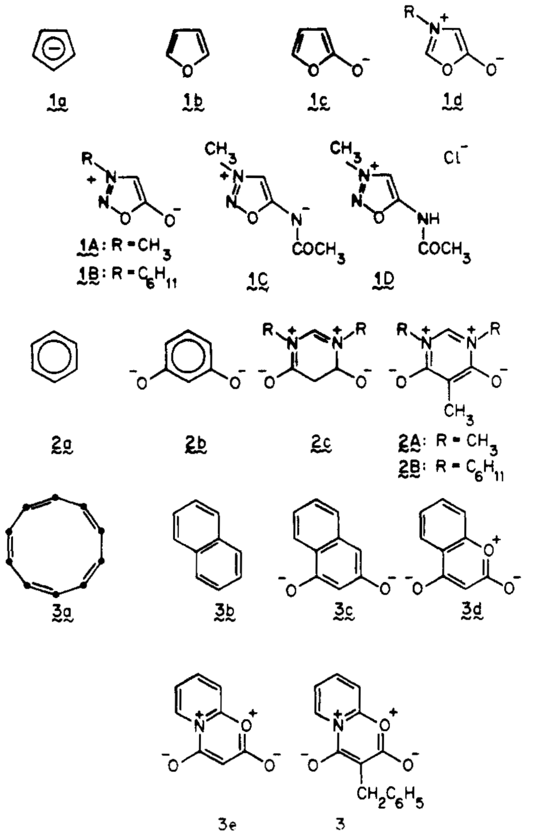


Figure 4. **2A**: MNDO bond lengths (Å) and angles (deg) and net atomic charges (π charges in parentheses).

Chart I



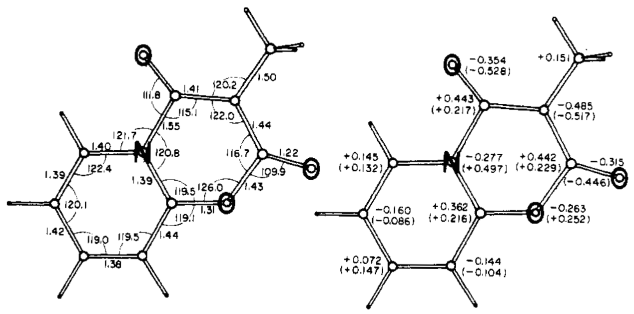


Figure 5. **3**: MNDO bond lengths (Å) and angles (deg) and net atomic charges (π charges in parentheses).

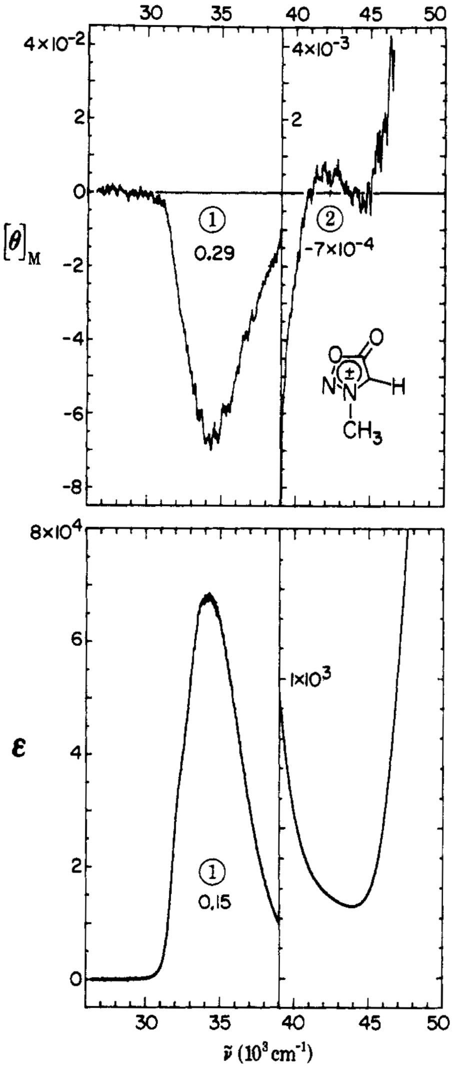


Figure 6. **1A**: UV (top) and MCD (bottom) spectra. Oscillator strengths and *B* terms ($10^{-3}\beta_e D^2/\mathrm{cm}^{-1}$) are indicated.

ments were wavelength-calibrated with use of a holmium oxide filter.[15] The dichrograph was calibrated at 290 nm with use of a solution of anhydrous *d*-camphorsulfonic acid (154.8 mg, prepared according to ref 16 without equilibration in air) in nanograde water (250 mL): $[\Theta]_{290} = 7775$ deg cm^2 dmol^{-1}.[17] Since this does not guarantee a correct calibration over the whole wavelength range of the instrument,[16] we checked the magnitude of the deviations at both shorter and longer wavelengths. Using a 1.33×10^{-3} M aqueous solution of D-pantolactone, we found $\Delta[\Theta]_{220} = -1\%$ at 220 nm, and using a 2.81×10^{-3} M aqueous solution of *d*-tris(ethylenediamine)cobalt(III) iodide monohydrate, we found $\Delta[\Theta]_{491} = -5\%$ at 491 nm.[18] The magnet was calibrated by using a 0.155 M aqueous solution of $CoSO_4 \cdot 7H_2O$ for which $[\Theta]_M = 6.2 \times 10^{-3}$ deg cm^2 dmol^{-1} G^{-1} at 510 nm.[19] The published MCD spectra of several organic samples such as benzene and naphthalene were then reproduced with an accuracy of about 10%.

The *B* terms and oscillator strengths were calculated from the measured spectra with use of formulas given previously.[20]

Calculations. These were performed by using MNDO[21]-optimized molecular geometries (planarity was assumed: this assumption was checked by an unconstrained optimization in the case of unsubstituted parent sydnone). Parameters for PPP calculations were those of ref 20. Both PPP and INDO/S[22]

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Table I. Spectra of Mesoionic Compounds

				ΔHOMO – ΔLUMO, eV	
compd	$\tilde{\nu}_{max}$, 10^3 cm^{-1}	f[a]	B, $10^{-3}\beta_e D^2/cm^{-1}$	MNDO	INDO/S
1A	34.1	0.15	0.29	1.81	1.57
	~42.0	...	(-7.10^{-4})		
1B	34.05	0.15	0.30	...	...
	~42.0	...	(−0.003)	...	...
1C	30.2	0.24	0.4	1.66	1.22
	41.5	0.18	−0.03		
1D	35.8	0.31	0.2	1.55	0.79
	[47.8]	...	...		
2A	31.0	0.04	0.5	0.90	0.97
	37.5 (sh)				
	38.3	0.1	−0.3		
	46.5	0.7	0.9		
2B	30.6	0.04	0.4	...	...
	36.9 (sh)				
	38.0	0.09	−0.4		
	44.8 (sh)				
	45.6	0.9	1.1		
3	27.9	0.1	0.5	1.54	1.72
	33.2 (sh)				
	34.6	0.02	0.2		
	37.1 (sh)				
	40.8	0.4	0.6		
	~47.0 (sh)	...	...		

[a] Oscillator strength.

calculations used only singly excited configurations, all in the former case and those from the ten highest occupied to the ten lowest unoccupied MO's in the latter case.

Results and Discussion

The MNDO-optimized geometries and calculated charges are shown in Figures 1–5. The bond lengths and angles are in fair agreement with experimental geometries of typical mesoionic compounds.[4] The net atomic charges and π charges agree with the current notions concerning the electronic structure of these heterocycles.

The spectral results are collected in Figures 6–10 and in Table I. The spectra of **1B** are essentially identical with those of **1A** and the spectra of **2B** with those of **2A** and are not shown.

The combined UV and MCD spectra suggest the assignment of two transitions in the accessible regions, as indicated in Figures 6–10. In each case, the lower energy transition has a positive and the next higher energy transition a much smaller negative B term. The relatively high UV intensities of these transitions leave little doubt that they are of $\pi\pi^*$ nature, except possibly for the second transition in **1A** and **1B**, seen only in the MCD spectrum and very weakly at that.

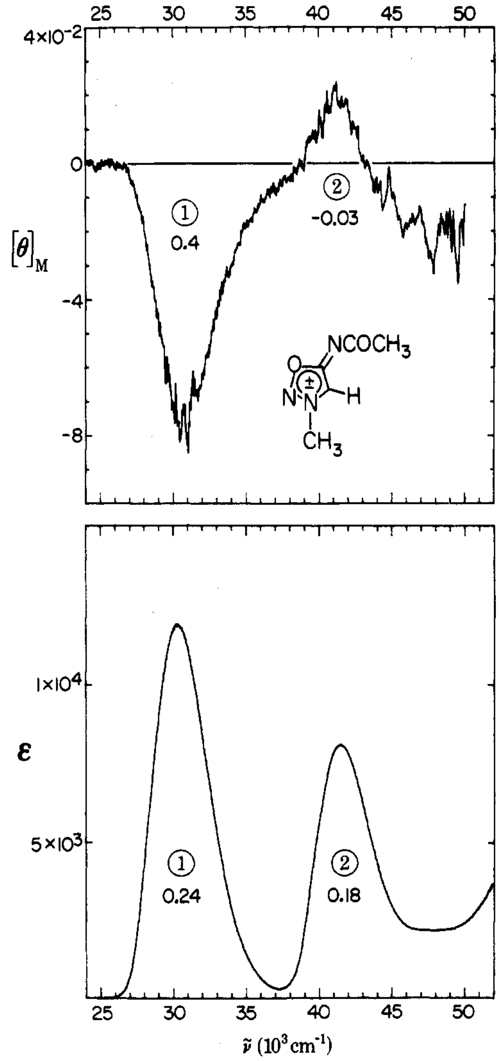

Figure 7. **1C**: UV (top) and MCD (bottom) spectra. Oscillator strengths and B terms ($10^{-3}\beta_e D^2/cm^{-1}$) are indicated.

In systems derived from $(4n + 2)$-electron perimeters, one expects two low-energy excited states of the L type, L_1 and L_2 in the order of increasing energy, followed at higher energies by two states of the B type. Inspection of the nature of the PPP and INDO/S wave functions for the lowest calculated states indeed suggests that the first two $\pi\pi^*$ states correspond to strongly perturbed L_1 and L_2 states of the perimeter. However, the actual numerical agreement of the calculated energies, intensities, and B terms with the observed values is poor, and the details are not given here. The difficulty with the PPP method is in the choice of parameters for the numerous heteroatoms present, many of which carry large charges. The problem with the INDO/S method is that it predicts the existence of a fair number of $n\pi^*$ states at relatively low energies. We have no evidence for their existence and suspect that the method underestimates their energies as it is known to do in other heterocycles.[23] The incorrect state ordering

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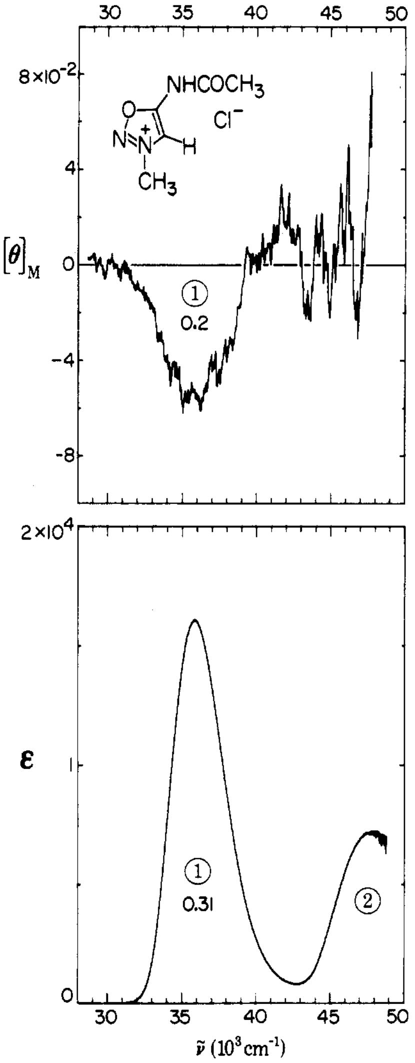

Figure 8. **1D**: UV (top) and MCD (bottom) spectra. Oscillator strengths and B terms ($10^{-3}\beta_eD^2/cm^{-1}$) are indicated.

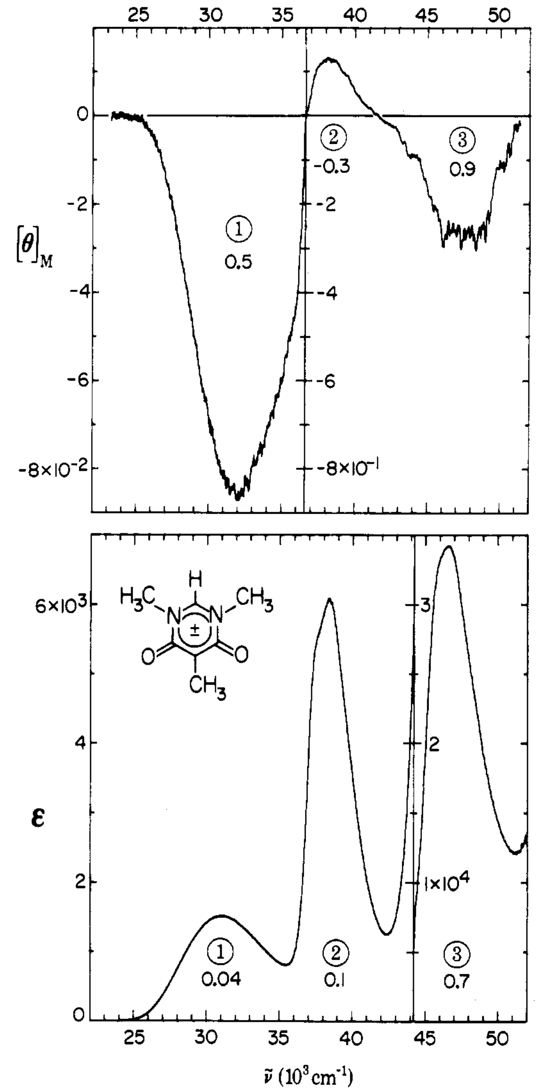

Figure 9. **2A**: UV (top) and MCD (bottom) spectra. Oscillator strengths and B terms ($10^{-3}\beta_eD^2/cm^{-1}$) are indicated.

then affects the INDO/S results for B terms and is at least partly responsible for the poor agreement between the calculated and observed MCD signs of $\pi\pi^*$ transitions. When it comes to quantitative or even semiquantitative treatment of UV and MCD spectra, the mesoionic compounds considered here, and presumably others, appear to be beyond the reach of the standard semiempirical methods of calculation.

While the disagreement of the observed MCD signs with those computed by the standard procedure is disappointing, it is perhaps of more interest to ask whether the signs can be understood in an intuitive manner without the need for a specific choice of semiempirical parameters. According to the simple perimeter model,[2] the B terms of both L bands should receive a positive contribution from magnetic mixing of the L states with the B states (μ^--contribution). Superimposed on this should be a μ^+-contribution due to the mutual magnetic mixing of the L states. This is only present if ΔHOMO, the energy difference between the highest two occupied π MO's derived from the perimeter, differs from ΔLUMO, the energy difference between the lowest two unoccupied π MO's derived from the perimeter. If ΔHOMO > ΔLUMO, the L_1–L_2 mixing provides a positive μ^+-contribution to the B term of the L_1 band and an equally sized but negative one to that of the L_2 band. Note that by definition the sign of the observed MCD peak is opposite to the sign of its B term. The deviation of ΔHOMO and ΔLUMO from zero also provides the L bands with absorption intensity.

Which case obtains is determined by the detailed nature of the perturbation that produces the molecule in question from the parent perimeter.[2] In systems derived from a charged perimeter such as **1**, the L_2 transition should have no intensity even if ΔHOMO and ΔLUMO are nonzero as long as they are equal, ΔHOMO = ΔLUMO. Perturbation of the kind that produces **2** is such that L_b (= L_1) would have no intensity if ΔHOMO = ΔLUMO (odd-soft chromophore). Perturbations leading to **3** are such that neither of the L states would be expected to have zero intensity if ΔHOMO = ΔLUMO (zero-soft chromophore).

Thus, within the perimeter model, the spectra in Figures 6–10 can be understood as follows: in **1A** and **1B**, ΔHOMO is somewhat larger than ΔLUMO, so that the positive μ^+-contribution combined with the μ^--contribution gives a distinct positive B term to the L_1 band, and the negative μ^+-contribution just barely overwhelms the μ^--contribution to yield a weakly negative resultant B term for the L_2 band. The difference ΔHOMO − ΔLUMO is insufficient to produce a distinct and intense L_2 band in absorption.

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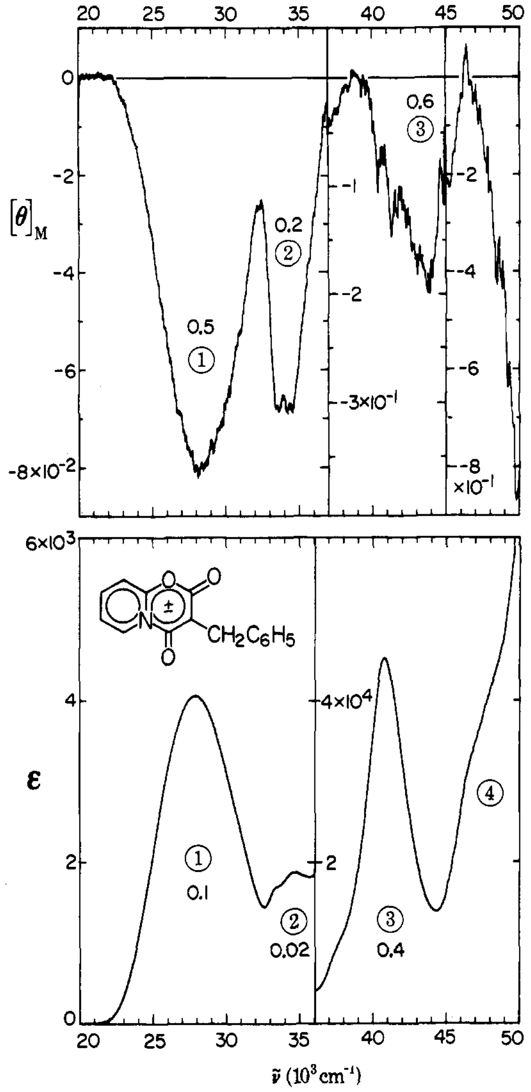

Figure 10. 3: UV (top) and MCD (bottom) spectra. Oscillator strengths and B terms ($10^{-3}\beta_e D^2/\text{cm}^{-1}$) are indicated.

When the ring substituent is a better π donor (**1C**), $-N^{-}-COCH_3$ rather than $-O^{-}$, the difference ΔHOMO − ΔLUMO should become more positive. The μ^{+}-contribution to the B term of L_1 should become more positive and that to the B term of L_2 more negative, as observed, and the absorption intensity apparently increases enough for this transition to produce a distinct band in the UV spectrum.

When the ring substituent is a poorer π donor (**1D**), the opposite changes occur. Then, the B term of L_1 should be less positive, as observed, and L_2 is hard to discern in MCD as well as UV spectrum.

MNDO and INDO/S calculations indeed predict positive values for ΔHOMO − ΔLUMO, which however do not always lie in the order required by the simple model. The origin of this positive ΔHOMO − ΔLUMO value can be traced along the series **1a** → **1A** and **2b** → **2A** using simple PMO[24] arguments and is seen to be primarily due to the splitting of the perimeter HOMO's by the strong donor substituents $-O^{-}$. In this respect, these mesoionic compounds resemble other monocyclic lactams such as the pyridones, which also have strongly positive B terms for their first $\pi\pi^*$ transition.[25]

Conclusions. MCD spectroscopy permits the identification of the L_2 transition even in those monocyclic mesoionic compounds where it is not apparent in the UV spectra. The signs of the B terms of the spectra and even their relative magnitudes in the series **1A–D** can be understood qualitatively within the framework of the simple perimeter model for $(4n + 2)$-electron perimeters, in terms of the positive sign of the orbital energy double difference ΔHOMO − ΔLUMO, which is readily derived by using the PMO theory. However, numerical calculations of the B terms using the semiempirical PPP and INDO/S methods with standard parameters do not provide satisfactory results for this class of molecules. Although better agreement might possibly be attained by an adjustment of semiempirical parameters, this does not strike us as a fruitful exercise.

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