Tetrahedron Vol. 38, No. 11, pp. 1571 to 1578, 1982.
Printed in Great Britain.

0040-4020/82/111571-08$03.00/0

MAGNETIC CIRCULAR DICHROISM OF CYCLIC π-ELECTRON SYSTEMS—25[1]

OXO DERIVATIVES OF INDAZOLE, BENZIMIDAZOLE AND PURINE

M. VAŠÁK,[2] J. W. DOWNING,[2] L. B. TOWNSEND[3] and J. MICHL[2]*
Department of Chemistry and Department of Biopharmaceutical Sciences, University of Utah, Salt Lake City, UT 84112, U.S.A.

(*Received in U.S.A.* 13 *April* 1981)

Abstract—The simple perimeter model combined with PMO theory and semimpirical calculations is used to rationalize the observed MCD spectra of a series of oxo derivatives of azaindoles, such as caffeine and xanthine. The MCD spectra indicate the presence of substantial amounts of the 9-H tautomers in aqueous solutions of xanthines.

The recently proposed[4-6] simple model for interpretation of magnetic circular dichroism of low-energy transitions in cyclic π-electron systems derived from a (4N+2)-electron perimeter has been tested successfully on several hydrocarbons derived from an uncharged perimeter, as well as their numerous heterocyclic and substituted analogs.[7-9] More recently, it has been reported to work quite satisfactorily for the indenide anion and its simple heterocyclic[10] and amino substituted[11] derivatives, all of which are derived from the charged perimeter, $C_9H_9^-$. The distinction between uncharged and charged perimeters is important since the theory suggests and so far, experiment confirms that the MCD spectra of the two classes of molecules exhibit different behavior upon substitution.

In the present paper, we apply the model to a group of compounds which are only rather remotely related to a simple perimeter, namely the oxo derivatives of azaindoles, with particular emphasis on the purines. Because of their fundamental biological importance, electronic spectroscopy of these compounds has already received a great deal of attention. It is not our purpose here to review all of the studies of their electronic structure. Suffice it to note the existence of a thorough discussion of their electronic states in connection with a comparison with semiempirical all-valence electron calculations[12,13] and the existence of previous MCD measurements on a few of the most important representatives of this group of compounds.[14,15] No MCD calculations on the presently investigated oxopurines appear to have been published, but the CNDO/S and INDO/S methods have been used to calculate the MCD effect in simpler purines[16] and have produced qualitative agreement with simple arguments based on the perimeter model.[10,11]

The meaningfulness of the correlation of the electronic states of oxopurines with those of their perimeter has been questioned.[12] Still, among all current spectroscopic tools, MCD probably is the one which most directly probes the nodal properties of molecular wavefunctions along the conjugated cyclic perimeter, and the application of the perimeter model appears worthwhile. In our spectra, we label the L_1 band as 1 and the L_2 band as 2. It has already been noted in Parts 6[7] and 10[8] of this series that the MCD spectra of analogous oxo derivatives of heterocycles derived from a 6-membered and a 10-membered perimeter, respectively, which are also only distantly related to their parent perimeter, can be understood in a very satisfactory manner using the simple model. The perturbation needed to derive the cyclic lactam structure from an annulene perimeter is a replacement of a -CH= group by the $-NH^+$= group and of one perimeter hydrogen by the $-O^-$ substituent. This implies an electron-withdrawing (+I) inductive effect at the position of the NH group and a very strong electron-donating (−E) mesomeric effect at the position of the carbonyl group. In studies of such lactams derived from benzene[7] and naphthalene[8] it was noted that the −E effect of $-O^-$ is even stronger than that of the $-NH_2$ group and is likely to affect orbital ordering in subdominant[6] positions of substitution and thus cause MCD sign switching. The present results further bear out this tendency and provide the first example of such a sign switch on a system derived from a charged perimeter.

RESULTS AND DISCUSSION

The measured absorption and MCD spectra are shown in Figs. 1–10. The calculated results for ππ* transitions obtained from π-electron (PPP) and all-valence-electron (INDO/S) calculations were very similar, at least for low-energy transitions. The agreement of calculated excitation energies with measured values was a little better for the INDO/S method. On the other hand, this method produces unrealistically low excitation energies for nπ* excited states: for most of the compounds, it predicts one or two such states at energies 5000–10,000 cm^{-1} below the first ππ* excitation. There is no experimental evidence for such transitions and we believe that the method can only be taken seriously for transitions of the ππ* type. Even then, magnetic mixing with a spurious low-energy nπ* state can affect the calculated B term of a nearby ππ* transition in an unrealistic way. In practice, this was noted only if the calculated energies of the nπ* and ππ* transitions were almost identical. Similar inadequacies in the current semiempirical spectroscopic all-valence-electron methods were noted previously.[17] For this reason, we have chosen the PPP results for display in Figs. 1–10.

In one case, 3-hydroxy-2-azaindole, the two methods of calculation agree less well and both sets of results are shown in Fig. 2. For this molecule, no spurious low-energy nπ* states are predicted by the INDO/S method.

Although the results calculated for ππ* states

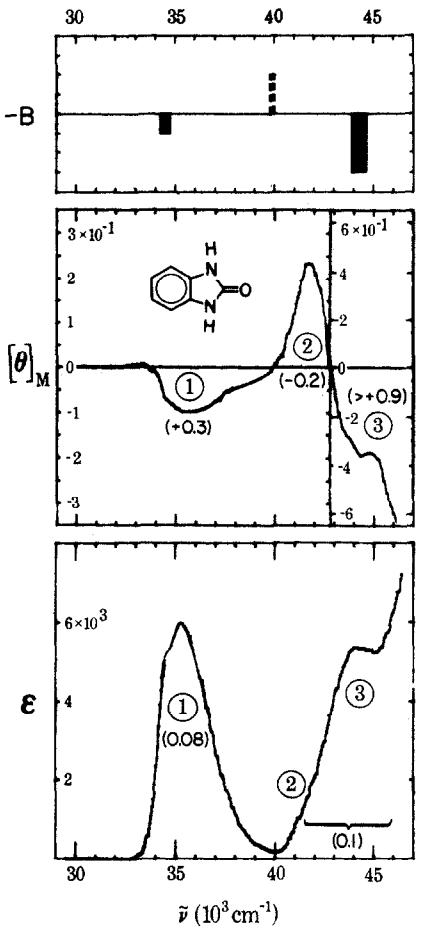


Fig. 1. 2-Hydroxybenzimidazole. Bottom: absorption (oscillator strengths given); center: MCD (B terms in units of $10^{-3}\beta_e D^2/cm^{-1}$); top: calculated $-B$ values are indicated by the length of the bars (short, below 1; medium, 1–5; long, greater than 5; in units of $10^{-3}\beta_e D^2/cm^{-1}$) and calculated oscillator strengths by their three grades of thickness (less than 0.1, 0.1–1, greater than 1). Solid bars indicate horizontal polarization and broken bars vertical polarization with respect to the formula as shown.

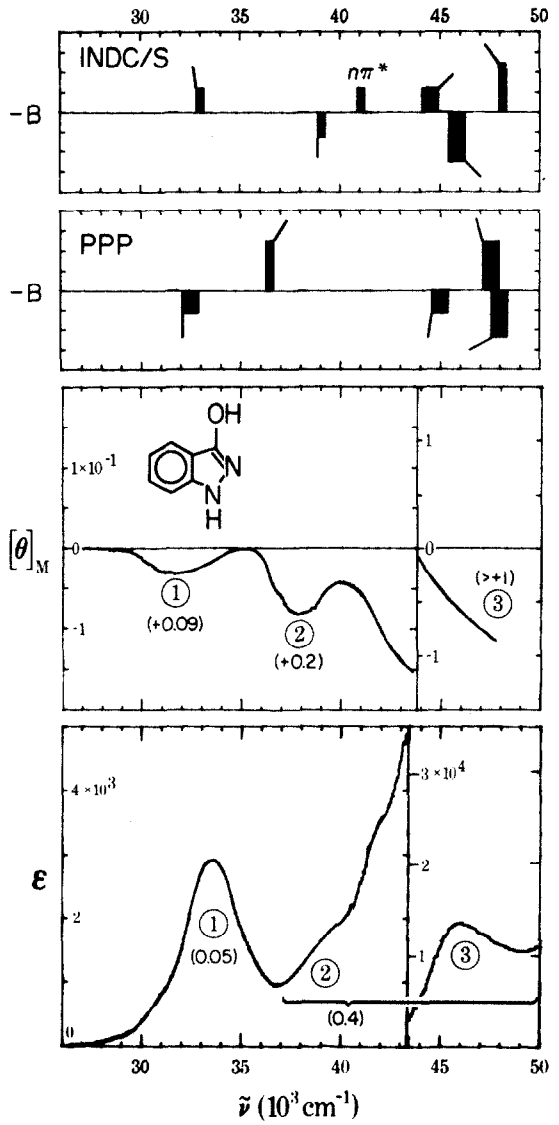
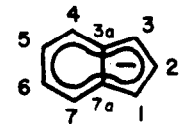


Fig. 2. 3-Indazolinone, See caption to Fig. 1. Calculated polarizations are indicated by directions of the flags with respect to the formula as shown.

generally are in very good agreement with the experimental spectra, our primary emphasis on the interpretation of the results lies elsewhere: we are interested in finding out whether the relation of the observed MCD signs to molecular structure can be understood in simple terms based on the perimeter model, which do not require the use of a computer. This approach relates the MCD signs to orbital energy differences[4–6] whose behavior as a function of structure can be understood by the use of simple perturbation MO theory (PMO[18]). The validity of the simple arguments was checked against the orbital energies calculated by the PPP, INDO/S, and Extended Hückel (EH) methods. The agreement was good except that the EH method has a tendency to exaggerate the magnitude of ΔLUMO somewhat. This is an understandable consequence of the explicit inclusion of overlap in the calculation.

The perimeter model. According to the simple model described in Refs. 4–6 and summarized qualitatively in Refs. 10 and 11, the MCD signs of the two low-energy L transitions and two higher energy B transitions in molecules derived from (4N + 2)-electron perimeters can be understood as resulting from two contributions. One of these, the μ^- contribution, provides small positive magnitudes to the B terms of transitions L_1 and L_2, one or both of which may actually vanish depending on the details of the structure, and larger contributions to the B terms of the B transitions, the lower one of which (B_1) is positive and the upper one (B_2) negative. If the splitting of the highest two occupied MO's (ΔHOMO) is equal in size to the splitting of the lowest two unoccupied MO's (ΔLUMO), the μ^- contribution is the only one present. If the two splittings are unequal, another potentially much larger term, μ^+, contributes to the B terms. It frequently dominates the B terms of the L transitions and sometimes even those of the B transitions. If the difference ΔHOMO–ΔLUMO is positive, the μ^+ contributions to the B terms of the four transitions have the signs, +, −, +, −, in the order of increasing transition energy (L_1, L_2, B_1, B_2). If the difference is negative, the signs are −, +, −, +, respectively.

In the parent indenide anion 1, ΔHOMO and ΔLUMO are approximately equal, i.e. 1 is a soft chromophore



I

(single-soft,[9] since it is derived from a charged perimeter, $C_9H_9^-$). In a soft chromophore, minor perturbations can destroy the delicate balance of ΔHOMO and ΔLUMO in either direction,[10,11] introducing μ^+ contributions with one or another set of signs. This sensitivity of MCD signs to perturbations provided the justification for coining the term "soft" chromophore. The effects of perturbations such as substitution on the relative size of orbital energy differences can usually be estimated from simple perturbation theory arguments,[18] permitting back-of-the-envelope predictions of MCD signs. Electron-donating mesomeric substituents (−E) act primarily on the energies of the occupied orbitals and affect ΔHOMO, electron-withdrawing mesomeric substituents (+E) act primarily on the energies of the vacant orbitals and affect ΔLUMO. A position of attachment μ in which $c^2_{-1\mu} > c^2_{-2\mu}$ ($c^2_{1\mu} > c^2_{2\mu}$) is referred to as +E-dominant (−E-dominant); a position in which $c^2_{-1\mu} < c^2_{-2\mu}$ ($c^2_{1\mu} < c^2_{2\mu}$) is called +E-subdominant (−E-subdominant). The position labels are abbreviated in symbols such as DS where the first letter indicates that the position is +E-dominant and the second letter shows that it is −E-subdominant. In a DS position, PMO-type considerations show that a +E substituent will increase ΔLUMO, and a weak −E substituent will decrease ΔHOMO, so that either type of substitution will cause ΔHOMO–ΔLUMO to decrease (become less positive or more negative). As the −E substituent in a −E-subdominant position becomes gradually stronger, it will reduce ΔHOMO until it reaches zero, whereupon it reverses the order of the two bonding orbitals, and then it will proceed to increase ΔHOMO again. This is a general expectation for substitution in a subdominant position and has been observed on several cyclic π-systems derived from an uncharged perimeter, e.g. for γ-substitution in the pyridinium cation,[19] where the weaker −E substituents -Cl and -OH cause ΔHOMO < ΔLUMO, but the stronger $-NH_2$ substituent already pushes the system beyond the borderline and produces ΔHOMO > ΔLUMO, as does the even stronger $-O^-$ substituent which converts the pyridinium cation into γ-pyridone.[7]

Inductive substituents act equally efficiently on the energies of the unoccupied and occupied orbitals and affect both ΔHOMO and ΔLUMO. To the first order in perturbation theory, their net effect at a position is given by $\Delta(\Delta HOMO-\Delta LUMO)/(-\Delta\alpha) = c^2_{2\mu} - c^2_{1\mu} + c^2_{-2\mu} - c^2_{-1\mu}$. Positions in which this quantity is negative are called I-dominant, those in which it is positive are I-subdominant. In the former, an electron-withdrawing substituent, or an electronegative heteroatom, causes ΔHOMO–ΔLUMO to become less positive or more negative, whereas in the latter, it causes ΔHOMO–ΔLUMO to become more positive or less negative. An electron-donating substituent has the opposite effect.

Aza-oxo derivatives of the indenide anion (1). In the indenide anion 1, the four distinct positions are of the types 1 = D, 2 = S, 4 = D and 5 = S both for −E and I substituents, but the sensitivity of positions 4 and particularly 5 is relatively small.[10] The experimentally observed heteroatom[10] and −E substituent[11] effects agree with expectations based on this classification. Even the strongest among the −E substituents investigated so far, $-NH_2$, does not reverse the bonding orbital ordering when introduced into the subdominant positions 2 or 5, even when it is aided by electronegative nitrogens in both positions 1 and 3 which also tend to lower preferentially the energy of the HOMO.

Figure 1 shows that such a reversal is finally achieved by the even stronger −E substituent, $-O^-$, assisted by pyrrole-like nitrogens in positions 1 and 3, as demonstrated by the +,− sequence of the B terms of the lowest two transitions in 2-hydroxybenzimidazole, believed to be present as the oxo tautomer.[20] The orbital crossover is also easily identified in numerical calculations. All three methods used here yield the orbital ordering a, s, −s, −a, with ΔHOMO > ΔLUMO, to be compared with the s, a, −s, −a, ordering in the indenide anion.[10]

The other simple monoxodiaza derivative of 1, 3-indazolinone, exists primarily as the 3-hydroxy-2-azaindole tautomer[20] in solution (Fig. 2). In deriving it from 1, one introduces the strongest perturbation first by placing the NH group in position 1. This is expected to produce ΔHOMO < ΔLUMO, and indole indeed exhibits the anticipated −,+ sequence of B terms for the L_1 and L_2 bands.[10] The two weaker perturbations will counteract the effect of the NH group. The OH group represents a −E substituent in a D position (3) and the aza nitrogen a +I substituent in an S position (2). It is thus hardly surprising that the μ^+ contribution appears to be absent in the MCD spectrum (Fig. 2), which has weak positive B terms for both L transitions as expected from μ^- contributions alone when ΔHOMO ≐ ΔLUMO. Of course, it would have been difficult to predict *a priori* that the cancellation of the substituent effects will be so nearly perfect. Calculations by the three methods used presently produce small but nonvanishing positive values for the ΔHOMO–ΔLUMO difference. We suspect that a more accurate calculation would be required to reproduce the experimental result exactly.

It is of interest to note that a different result would be expected for the carbonyl tautomer, 3-oxoindazoline. The replacement of the −E substituent -OH by the much stronger donor, $-O^-$, in the D position 3, and of the aza nitrogen by the stronger azonia nitrogen $=NH^+-$ in the S position 2 should both contribute to an increase of ΔHOMO relative to ΔLUMO. This PMO argument is fully corroborated by all three kinds of calculations performed. We would therefore expect a sizeable positive B term for the first band of the carbonyl tautomer, followed by a sizeable negative term for the second band. This kind of result indicates the potential usefulness of the MCD technique in the study of tautomerism of heterocycles related to 1.

All other compounds presently investigated are oxo derivatives of purine. Their spectra and formulas are given in Figs. 3–10. Judging by the outcome of a cmr study of hypoxanthine and related purines,[21] the first four among these (Figs. 3–6) are likely to correspond to tautomeric mixtures of 7-H purines, which formally are 3,4,6-triazaindoles with oxo groups in indole positions 7 and mostly also 5, and of 9-H purines, which are 3,5,7-triazaindoles with oxo groups in indole position 4 and mostly also in position 6. Both structures are shown in the figures, the former labeled A and the latter B. All spectra exhibit fairly strong positive B terms for the first transition and negative B terms for the second transition.

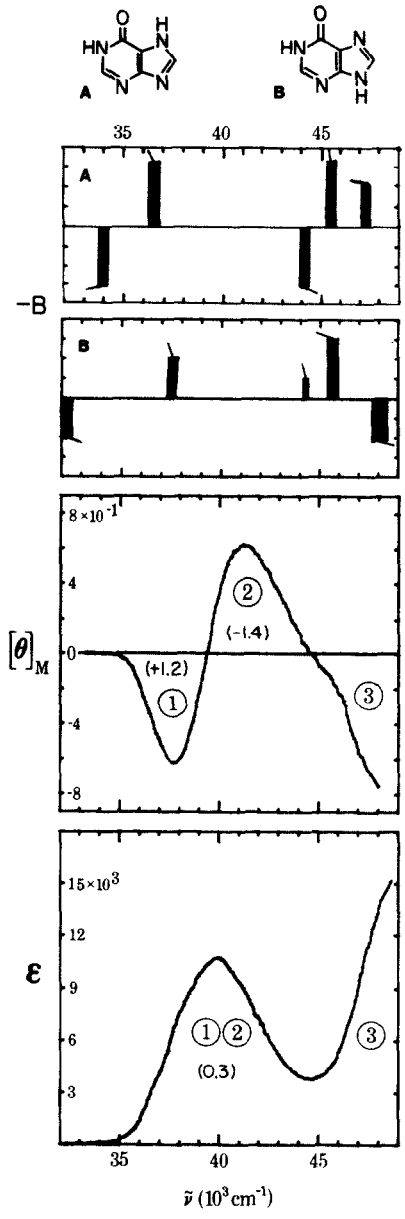
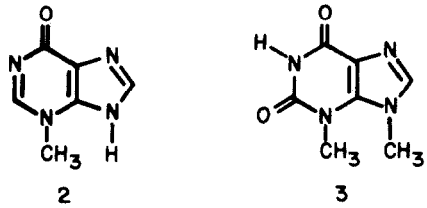


Fig. 3. Hypoxanthine. See captions to Figs. 1 and 2.

The same pattern is observed with the closely related previously studied[15] 3-methylhypoxanthine **2** (only one tautomeric structure is shown) and 3,9-dimethylxanthine **3**.



2 **3**

The results agree with our numerical calculations and with expectations based on simple PMO-type arguments along the lines discussed in some detail in Ref. 11. However, with the exception of hypoxanthine, this is true only if we assume the presence of substantial amounts of the 9-H tautomers. A – E substituent on **1** in the dominant position 4 is expected to induce ΔHOMO > ΔLUMO and it is already known[11] that the four nitrogens present in the purine skeleton, three of which oppose this tendency, do not prevail when the substituent is NH_2, i.e. in adenine, which exhibits a +,– pattern for its B terms. In hypoxanthine (Fig. 3), there would be even less reason for them to prevail than in adenine since $-O^-$ is a stronger donor than $-NH_2$ and the one nitrogen in position 5 which is actually helping to increase ΔHOMO relative to ΔLUMO is now more effective (pyrrole-like rather than pyridine-like). Thus, a clear +,– pattern in 9-H hypoxanthine must be expected, and is observed for the tautomeric mixture. The fact that the addition of another $-O^-$ substituent in position 6 and the conversion of another nitrogen in position 7 into a pyrrole-like one, which produces xanthine (Fig. 4), has

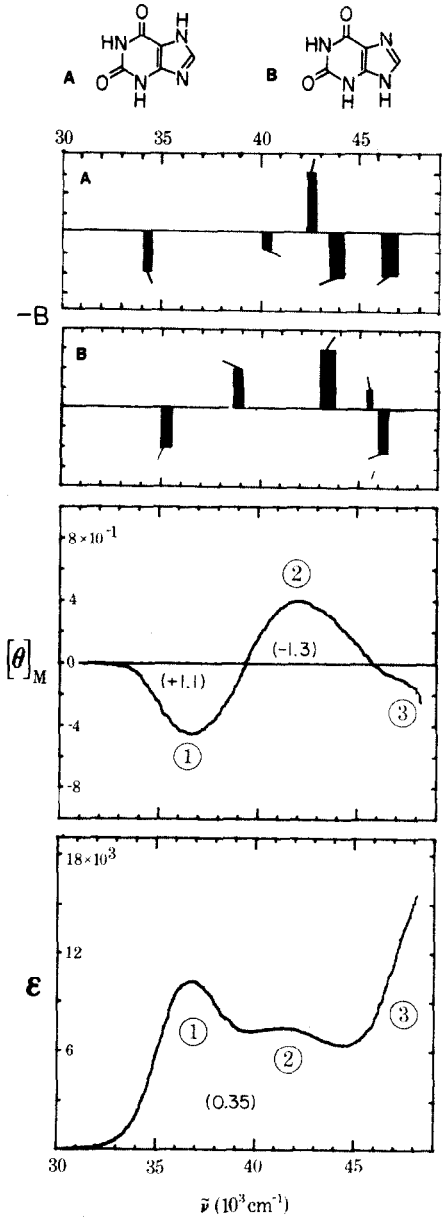


Fig. 4. Xanthine. See captions to Figs. 1 and 2.

relatively little effect, is compatible with expectations based on Table 3 of Ref. 11.

The reported[15] spectrum of **2** contains an additional negative MCD band at 234 nm. We suspect that this is due to the presence of a tautomer since it is absent in a cyclonucleoside with an otherwise similar chromophore.[15] It also disappears upon protonation, which enhances greatly the B terms of both L transitions. We take this to mean that protonation of an abundantly present tautomer **2** occurs in the position *ortho* to the CO, i.e. on the nitrogen which is helping to make ΔHOMO–ΔLUMO positive. Protonation on the aza N in the 5-membered ring or on the oxygen should have the opposite effect on the MCD spectrum. The proposed protonation ortho to the −E substituent is completely analogous to the protonation of 9-methyladenine discussed in Ref. 11, which also enhances the already present +,− pattern of B terms.

The next two compounds (Figs. 7 and 8) are likely to have tautomeric structures which can be viewed equally well as 3,5,7-triazaindoles or 3,4,6-triazaindoles. Their MCD spectra are very similar to those of the preceding group of compounds and the sign pattern of the B terms is +,−. This is in good agreement with our calculations which produce ΔHOMO > ΔLUMO and the correct signs for the B terms. The calculated PPP transition energies shown in the figures are rather poor, but this is hardly surprising for a computation performed without any parameter optimization (e.g., all resonance integrals are equal) on a molecule with such a large number of heteroatoms. The INDO/S energies agree a little better. The complexity of the substitution pattern, the presence

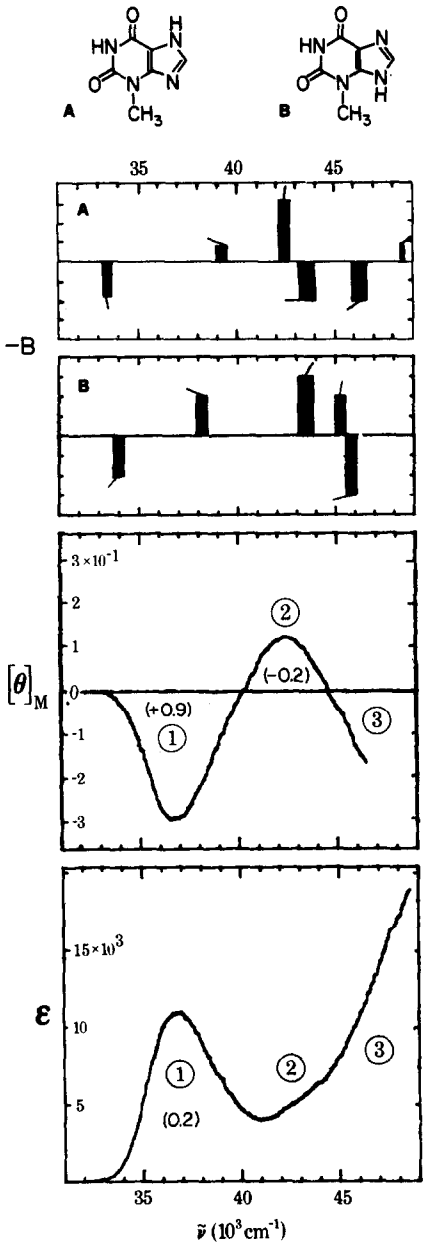


Fig. 5. 3-Methylxanthine. See captions to Figs. 1 and 2.

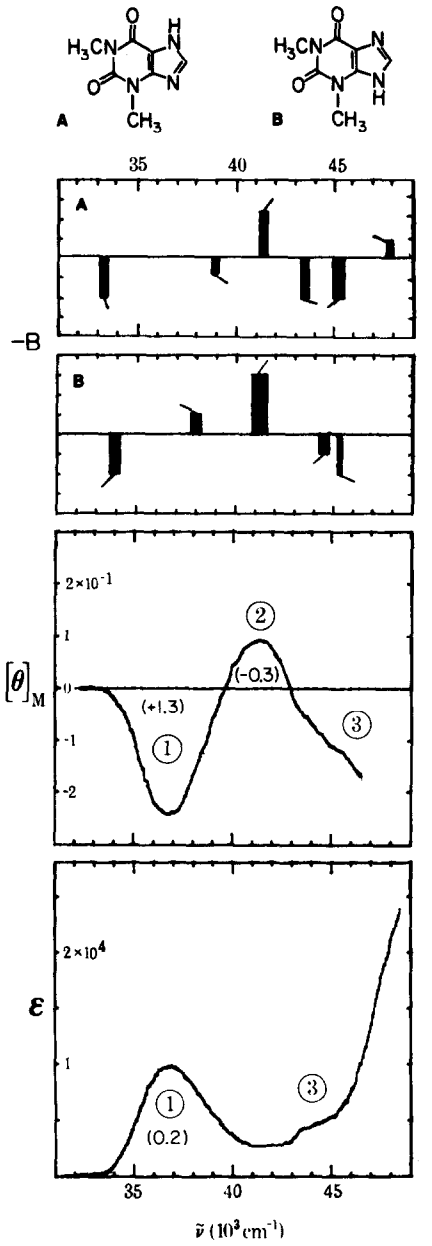


Fig. 6. Theophylline. See captions to Figs. 1 and 2.

of strong −E substituents in both S and D positions, and the absence of symmetry make it difficult to account for the order ΔHOMO > ΔLUMO by PMO-type arguments in a compelling way for these two compounds.

Finally, the two oxopurines which must be viewed as 3,4,6-triazaindoles (Figs. 9 and 10) have distinctly smaller positive B terms for both L transitions. This is in general agreement with our calculations, which yield approximately equal ΔHOMO and ΔLUMO, but not always exactly enough to reproduce the experimental signs of both bands. A comparision of these two structures, theobromine (Fig. 9) and caffeine (Fig. 10) with those of variously methylated xanthines (Figs 4–6) shows that they are almost identical with that of the 7-H tautomers of the latter and therefore differ from their 9-H tautomers primarily by interchange of heteroatoms in postions 1 and 3. A comparison of the spectra again indicates quite strongly that substantial amounts of the 9-H tautomers must be present in aqueous solutions of the xanthines (this contradicts the view expressed in Ref. 20 but is in line with the results of Ref. 21).

The direction of the difference in the ΔHOMO–ΔLUMO value in theobromine and caffeine, which is almost zero, and of the 9-H xanthines, which is clearly positive, is accounted for easily by an argument of the PMO type, albeit only in a qualitative fashion. The argument has two parts. The first is identical with the rationalization of the difference in the signs of the B terms of the L transitions in 4-aminoindole and 7-aminoindole given in Ref. 11: Table 3 of Ref. 11 shows that the tendency of a −E substituent in the 4 position of indole to impose ΔHOMO > ΔLUMO against the efforts of the NH heteroatom in position 1 to impose the opposite is considerably higher than that of the same −E substituent in the 7 position. The second part is identical with the rationalization of the difference in the magnitudes of the B terms of the L transitions in 7-methylpurine and 9-methylpurine given in Ref. 10: Table 2 of Ref. 10 shows that a +I heteroatom in the position 5 of indole has a tendency to produce ΔHOMO > ΔLUMO against the efforts of the NH heteroatom in position 1 to impose the opposite, while the same +I heteroatom in the indole position 6 has essentially no effect. Indeed, 5-azaindole is predicted[10] to exhibit a sign pattern (+,−) opposite to that of indole itself (−,+). The MO coefficients listed in Table 2 of Ref. 10 show also that a −E substituent in the subdominant position 5 of indole will tend to decrease ΔHOMO while it will have little effect in the neutral position 6.

Although the above PMO reasoning is admittedly crude and qualitative, it is satisfying to note that the structural features which have been identified as responsible for the observed differences between caffeine or theobromine on the one hand, and xanthine or methylxanthine on the other hand, are the same as those which are held responsible for the observed differences be-

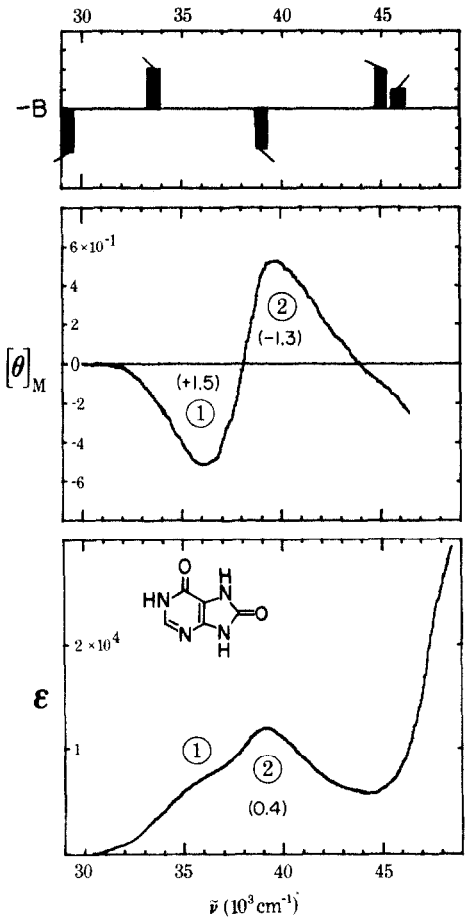


Fig. 7. 2,4-Dioxypurine. See captions to Figs. 1 and 2.

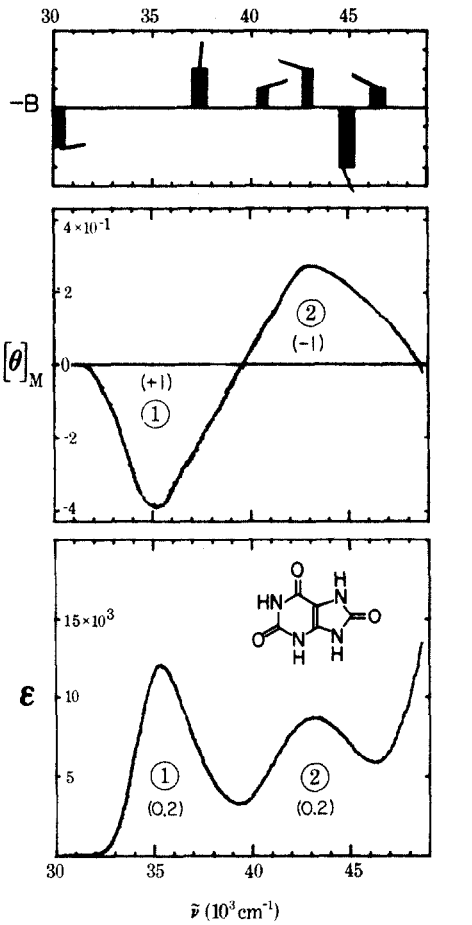


Fig. 8. Uric acid. See caption to Fig. 1.

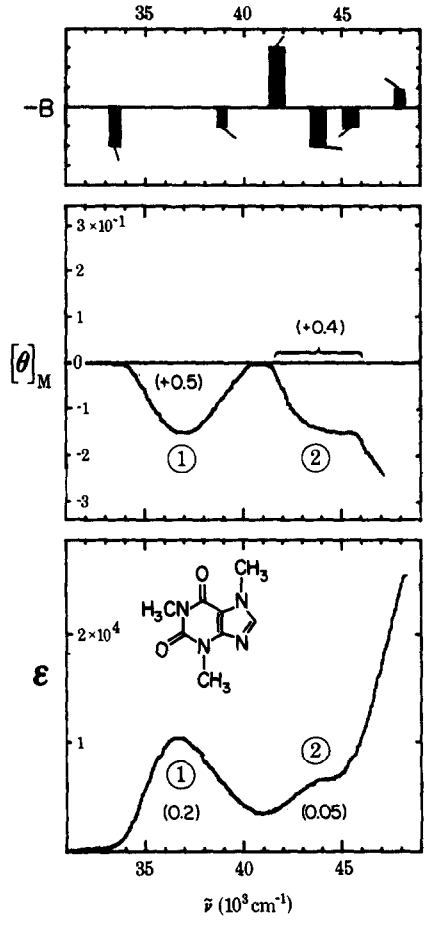


Fig. 9. Theobromine. See captions to Figs. 1 and 2.

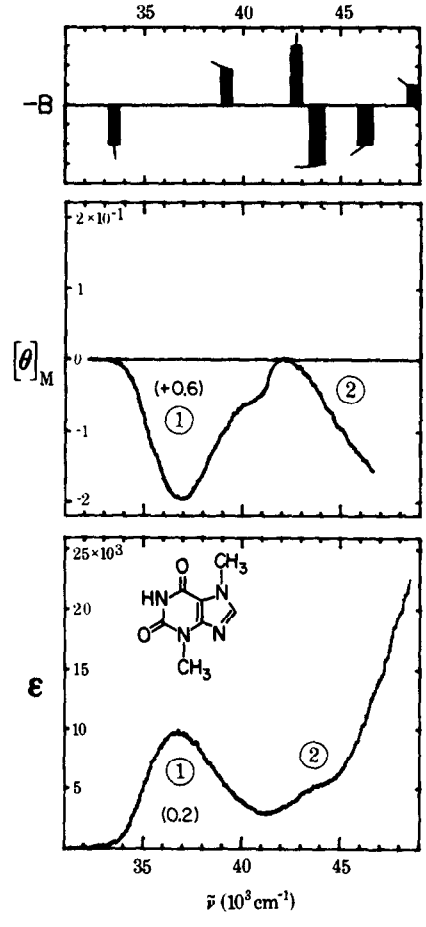


Fig. 10. Caffeine. See captions to Figs. 1 and 2.

tween 4-aminoindole and 7-aminoindole, and between 7-methylpurine and 9-methylpurine. The significant deviation of the MCD spectra of caffeine and theobromine from those of the outer oxopurines thus forms a part of much wider structural pattern.

CONCLUSIONS

The simple model of Refs. 4–6 permits a qualitative rationalization of trends in the long-wavelength region of the MCD spectra of oxo derivatives of azaindoles. Frequently, the requisite relative values of ΔHOMO–ΔLUMO can be estimated using PMO theory, but in some cases, it appears to be necessary to perform numerical calculations. The PMO approach offers the advantage of identifying the critical structural features which govern the MCD spectra. A quantitative evaluation would undoubtedly require a much more complex theory.

The MCD spectra indicate strongly that the 9-H tautomers are present in substantial amounts in aqueous solutions of hypoxanthine, xanthine, and related purines. It is quite likely that a more exhaustive MCD study using a series of solvents would provide detailed information about tautomeric and protonation equilibria for this class of molecules.

EXPERIMENTAL PART AND CALCULATIONS

The samples of 2-hydroxybenzimidazole and 3-indazolinone were commercial, the others were obtained from the collection of one of us (L.B.T.). They were purified by gradient sublimation and the spectra were measured in neutral aqueous soln except for uric acid for which pH was adjusted to 3 by addition of HCl, and for 2-hydroxyimidazole and 3-indazolinone, which were measured in acetonitrile. The measurements were done using techniques of Ref. 9. PPP calculations were performed as in Ref. 9 using the lower value of 9.1 eV for A_{N^+}, but including next-nearest-neighbor interactions included in the evaluation of the matrix elements of the magnetic dipole moment operator similarly as noted in Ref. 11. They were repeated without these interactions, but essentially identical results were obtained. Extended Hückel calculations were performed using the FAKE variation of the method,[22] and INDO/S calculations were performed as described in Ref. 23. No INDO/S calculations were performed for theobromine due to program limitations.

Acknowledgements—This work was supported by U.S. Public Health Service Grant GM-21153. We are grateful to Prof. Henry Eyring for a kind permission to use his MCD spectrometer and to Mr. B. Sinković for help with the calculations. One of us (M.V.) acknowledges support from the Swiss National Foundation.

REFERENCES

[1]Part 24: P. B. Pedersen, E. W. Thulstrup and J. Michl, *Chem. Phys.* **60**, 187 (1981).
[2]Department of Chemistry.
[3]Department of Biopharmaceutical Sciences. Present address: College of Pharmacy, University of Michigan, Ann Arbor, MI 48109, U.S.A.
[4]J. Michl, *J. Am. Chem. Soc.* **100**, 6801 (1978).
[5]J. Michl, *Ibid.* **100**, 6812 (1978).
[6]J. Michl, *Ibid.* **100**, 6819 (1978).

[7]I. Jonáš and J. Michl, *Ibid.* **100**, 6834 (1978).
[8]D. Otteson and J. Michl, *Ibid.* **100**, 6857 (1978).
[9]A. Castellan and J. Michl, *Ibid.* **100**, 6824 (1978), and the immediately following series of papers.
[10]M. A. Souto, S. L. Wallace and J. Michl, *Tetrahedron* **36**, 1521 (1980).
[11]S. L. Wallace and J. Michl, *Ibid.* **36**, 1531 (1980).
[12]W. Hug and I. Tinoco, Jr., *J. Am. Chem. Soc.* **95**, 2803 (1973).
[13]W. Hug and I. Tinoco, Jr., *Ibid.* **96**, 665 (1974).
[14]W. Voelter, R. Records, E. Bunnenberg and C. Djerassi, *Ibid.* **90**, 6163 (1968).
[15]W. Voelter, G. Barth, R. Records, E. Bunnenberg and C. Djerassi, *Ibid.* **91**, 6165 (1969).
[16]R. E. Linder, G. Barth, E. Bunnenberg and C. Djerassi, *Ibid.* **46**, 79 (1977); A. Kaito and M. Hatano, *Bull. Chem. Soc., Japan* **53**, 3064 (1980).
[17]M. Cignitti and L. Paoloni, *Theor. Chim. Acta* **25**, 277 (1972); A. Kaito and M. Hatano, *Bull. Chem. Soc., Japan* **53**, 3069 (1980).
[18]M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*. Plenum Press, New York (1975).
[19]S. L. Wallace, A. Castellan, D. Muller and J. Michl, *J. Am. Chem. Soc.* **100**, 6828 (1978).
[20]J. Elguero, C. Marzin, A. R. Katritzky and P. Linda, *The Tautomerism of Heterocycles*. Academic Press, New York (1976).
[21]M.-T. Chenon, R. J. Pugmire, D. M. Grant, R. P. Panzica and L. B. Townsend, *J. Am. Chem. Soc.* **97**, 4636 (1975).
[22]F. E. Harris, A. Trautwein and J. Delhalle, *Chem. Phys. Lett.* **72**, 315 (1980).
[23]R. West, J. W. Downing, S. Inagaki and J. Michl, *J. Am. Chem. Soc.* **103**, 5073 (1981); J. Ridley and M. Zerner, *Theor. Chim. Acta* **32**, 111 (1973); see also Ref. 16.