Moreover, the distance found between neighboring columns (d = 34 Å) is quite in accordance with the expected molecular parameters of the constituting molecules. In the large-angle region, X-ray diffraction measurements also show two broad and diffuse rings. The first one corresponds to a spacing of 5 Å, which is characteristic of paraffinic moieties in a disordered state. The second ring at 3.8 Å is presumably related to the stacking of the macrocyclic subunits within the columns. The density of the complex I_b has been measured by a flotation technique in binary mixtures water/dimethylformamide ($\rho = 0.98 \pm 0.01$ g cm^{-3}). Knowing the periodicity of the hexagonal lattic previously determined, it is possible to calculate the mean stacking distance of the molecules along the axis of the columns. The value of 3.7 Å which is found in that way is in good agreement with the distance obtained from the X-ray patterns. The structure of the mesophase seems to remain unchanged from about 60 to 300 °C. As far as we know no other discotic phase is stable over such an extended range of temperature.

In conclusion, a new type of discotic mesophase has been prepared and characterized. Metallophalocyanine subunits are used to constitute their rigid core. Doped liquid crystals have been prepared by recrystallizing the substituted phthalocyanine from heptane containing small amounts of iodine. Preliminary electron spin resonance measurements indicate a good mobility of the charge carriers inside each column. Conductivity studies are under progress to further elucidate the electrical properties of these new mesophases.

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Registry No. Ia, 82731-99-5; Ib, 82732-00-1.

Electron Transmission Spectroscopy of 1,3,5-Hexatriene: Isomeric Differences in π^* Orbital Energies

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We report here the observation of a large (0.55 eV) difference in the energies of the second π^* anion states of *cis*- and *trans*-1,3,5-hexatriene. This finding is of particular interest since photoelectron spectroscopy indicates that each of the three π ionization potentials (IP) of the two isomers agree respectively to within 0.10 eV.[1] Similarly, optical spectroscopy has revealed little difference in those $\pi \rightarrow \pi^*$ excitation energies of the two isomers which have been observed.[2]

In the present investigation we employ electron transmission spectroscopy (ETS)[3] to determine the gas-phase electron affinities (EA) of *cis*- and *trans*-hexatriene.[4] In Figure 1 we display the electron transmission spectra of these compounds, plotting the derivative of the electron beam current passing through the gas cell as a function of electron impact energy. In the derivative format the vertical attachment energies, that is, −EA, correspond to the vertical midpoints between adjacent dips and peaks. Within the context of Koopmans' theorem these electron affinities correspond to the negatives of the energies of the unoccupied orbitals, in the same way that the IP's are related to the energies of the filled orbitals. The energy resolution in this study is ≈0.04 eV, and the relative EA's should be accurate to ±0.03 eV.[5]

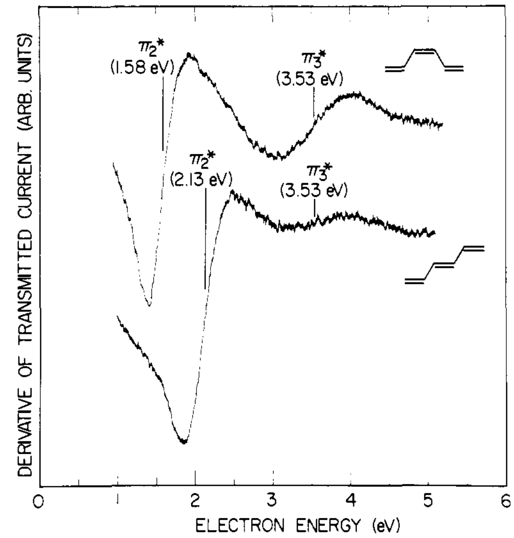

Figure 1. Derivative of transmitted current as a function of electron energy in *cis*- and *trans*-1,3,5-hexatriene. The vertical lines indicate the most probable attachment energies.

As shown in Figure 1, two anion states are observed in each molecule. From simple molecular orbital considerations one expects three low-lying π^* orbitals and hence three anion states. The energies of anion states in ethylene and butadiene[6] suggest that the ground-state anion of hexatriene is stable and hence inaccessible to study by ETS. We therefore assign the two observed features in the spectra to the second and third anion states, $^2B_1$ and $^2A_2$ for the cis species, assuming a planar C_{2h} structure, and ^2A_u and ^2B_g for the trans C_{2v} structure.

The most striking difference between the ET spectra of the two isomers is that the energy of electron attachment into the b_1 orbital of the cis isomer is 0.55 eV lower than that of the corresponding a_u orbital of the trans isomer.[7] To aid in the interpretation of these results it is useful to refer to the π^* MO's of the cis isomer (Chart I).[8]

Of the three π^* MO's, the $b_1(\pi^*_2)$ orbital has the largest charge densities on the C_2 and C_5 atoms. We propose therefore that the stabilization of the π^*_2 orbital of the cis isomer relative to that of the trans isomer is due to the C_2–C_5 bonding interaction. However, since the second π MO's also have substantial coefficients on C_2 and C_5, this picture would lead one to expect a sizable energy difference in the second π IP's of the two isomers, in contradiction to experiment. This objection is resolved, we contend, by noting that the anion wave functions are much more diffuse than those in the neutral molecule, greatly enhancing long-range interactions.

[†] John Simon Guggenheim Memorial Fellow.

(1) Beez, M.; Bieri, G.; Bock, H.; Heilbronner, E. *Helv. Chim. Acta* **1973**, *56*, 1028.

(2) Gavin, R. M., Jr.; Rice, S. A. *J. Chem. Phys.* **1974**, *60*, 3231.

(3) Sanche, L.; Schulz, G. J. *Phys. Rev. A* **1972**, *5*, 1672. Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

(4) The cis and trans mixture obtained from Aldrich Chemical Co. was separated on a 1 m 20% β,β'-oxydipropionitrile column (100/120 mesh Chromosorb P).

(5) Absolute energies are determined by reference to the 11.098-eV temporary anion state of argon: Brunt, J. N. H.; King, G. C.; Read, R. H. *J. Phys. B* **1977**, *10*, 1289.

(6) Burrow, P. D.; Jordan, K. D. *Chem. Phys. Lett.* **1975**, *36*, 594.

(7) Electron diffraction studies indicate that the trans isomer is planar and that the cis isomer is slightly nonplanar with a dihedral angle for twisting about the central double bond of 10°. See: Traetteburg, M. Acta. Chem. Scand. **1968**, *22*, 628, 2294. Theoretical calculations, e.g. ref. 15, indicate that both isomers are planar. In any case, twisting in the cis isomer would destabilize the second π^* orbital.

(8) See, for example; Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

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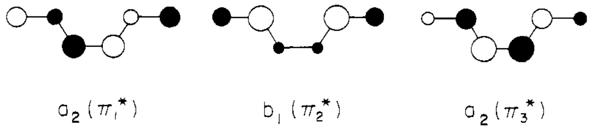
Chart I



Support for the above interpretation is provided by ab initio minimal (STO-3G) and split-valence (3-21G) basis set calculations[9] on *cis*- and *trans*-hexatriene. With the minimal basis set, long-range through-space interactions are not possible, while such interactions are possible with the split-valence basis set. The 3-21G calculations predict, in good agreement with experiment, that the second π^* orbital of the cis isomer is 0.41 eV below that of the trans isomer and that the π orbital energies agree to 0.09 eV. At the STO-3G level the second π^* orbital of the cis isomer is only 0.16 eV more stable than that of the trans. The 3-21G calculations further predict that the first π^* orbital energy is essentially the same for the two isomers and that the third π^* orbital is stabilized by 0.38 eV in the trans isomer. Unfortunately the latter prediction cannot be verified experimentally because of the small size of the π^*_3 structure and its overlap with the π^*_2 feature in the spectrum of the trans isomer.

We note that the importance of the increased diffuseness of anion wave functions has been discussed previously in various contexts.[6,10-12] In particular, we note that calculations by Staley et al.[12] have shown that the C_1–C_4 interaction in the first π^* orbital of *cis*-butadiene increases as the basis set is made more diffuse and that this π^* orbital is expected to be more stable in the cis than in the trans isomer. ETS studies on cyclic dienes[12,13] have provided experimental evidence of the importance of the C_1–C_4 interaction in these compounds. The present measurements, however, show directly that certain electron affinities will be appreciably different in cis and trans isomers. Such effects may be anticipated in the first and third π^* orbitals of 1,3,5,7-octatetraene, for example.

The role of such long-range through-space interactions on particular electronic states in the neutral molecule remains to be assessed. The available experimental data[2] on the excitation energies of *cis*- and *trans*-hexatriene fail to display appreciable differences, and large basis set calculations are available only for the trans isomer. The lowest dipole forbidden transition, in which one might expect to see a difference in the excitation energies of the two isomers, has not yet been observed or, at least, not yet unambiguously assigned.[14]

Finally, since the cis isomer of the *neutral* molecule is expected to be only slightly less stable than the trans, 0.13 eV according to force field calculations,[15] the present results indicate that the second *anion* state of the cis structure will be appreciably more stable, ~0.4 eV, than the trans.

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Registry No. *cis*-1,3,5-Hexatriene, 2612-46-6; *trans*-1,3,5-hexatriene, 821-07-8.

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(9) The calculations were performed by using the GAUSSIAN 82 program: DeFrees, D. J.; Levi, B. A.; Pollak, S. R.; Hout, R. F., Jr.; Hehre, W. J., to be submitted for publication.

(10) Jordan, K. D.; Burrow, P. D. *Chem. Phys.* **1980**, *45*, 171. Chiu, N. S.; Burrow, P. D.; Jordan, K. D. *Chem. Phys. Lett.* **1979**, *68*, 121. Burrow, P. D.; Ashe, A. J., III; Bellville, D. J.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 425.

(11) Staley, S. W.; Giordan, J. C.; Moore, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 3638.

(12) Staley, S. W.; Bjorke, M. D.; Giordan, J. C.; McMillan, M. R.; Moore, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7057.

(13) Giordan, J. C.; McMillan, M. R.; Moore, J. H.; Staley, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 4870.

(14) Hudson, B.; Kohler, B. *Ann. Rev. Phys. Chem.* **1974**, *25*, 437.

(15) Tai, J. C.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *83*, 7928.

On the Origins of the Blue Shift of the Carbonyl n–π^* Transition in Hydrogen-Bonding Solvents

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In hydrogen-bonding solvents the carbonyl n–π^* transition undergoes a blue shift of some 0.13–0.25 eV. Traditionally,[1-3] this shift has been regarded as due to the lowering of the ground-state energy by hydrogen bonding, the excited state supposedly showing little or no hydrogen bonding. (The possible influence of geometry changes was considered by Pimentel,[2] although this aspect seems to have received little attention recently.) Assuming that only the ground-state energy is lowered appreciably by hydrogen bonding, the T_e value of the n–π^* transition would be increased by the hydrogen-bond energy, with which the blue shift is then identified. A number of theoretical calculations appear to support this viewpoint.[4,5]

Recently, however, Beecham and co-workers have advanced a different interpretation of the blue shift in α,β-unsaturated ketones.[6,7] CD spectra, in which the vibrational structure of the n–π^* band was resolved, were obtained; in these spectra the blue shift arises entirely (to within 0.004 eV) from intensity redistribution among vibrational subbands. These observations are incompatible with the traditional viewpoint outlined above: the absence of a shift in T_e implies that the excited state remains hydrogen bonded and a blue shift occurs because the geometries of the ground and excited states of the solute are affected differently by hydrogen bonding. A model calculation was used in ref 7 to predict an extension of the excited state carbonyl CO bond due to hydrogen bonding.

The purpose of the present study is to demonstrate that even in the simplest carbonyl excited state a hydrogen bond is formed, and to advance an explanation for the blue shift based on geometry changes on hydrogen bonding. The system studied is formaldehyde–water. As the molecules studied by Beecham and Hurley[6] remain planar in their excited states, only planar geometries were considered in this work. This also facilitates comparison with the work of Del Bene.[4] Within this restriction, the geometries of $\tilde{X}(^1A_1)H_2CO$, $\tilde{A}(^1A_2)H_2CO$, $\tilde{X}(^1A_1)H_2O$, $\tilde{X}(^1A')H_2CO$–H_2O, and $\tilde{A}(^1A'')H_2CO$–H_2O were fully optimized by using SCF gradient techniques.[8] Labeling of atoms for reference is shown in Figure 1. A double ζ Gaussian basis[9] augmented with one set of polarization functions ($\alpha_d(C) = 0.7$, $\alpha_d(0) = 1.2$, $\alpha_p(H) = 0.8$) was used on each atom. All calculations were performed with the MOLECULE program system[10] as implemented on the CSIRONET Cyber 70/Model 76. Geometry parameters are converged to at least the figures given.

The optimized $\tilde{X}$- and $\tilde{A}$-state geometries of H_2CO–H_2O are given in Table I, together with the optimized values for the free solute and solvent. Hydrogen-bond energies (E_H), computed by using a counterpoise correction for superposition errors,[11] are also given; they show clearly that a strong hydrogen bond exists in the $\tilde{A}(^1A'')$ state. Noteworthy is the large CO_1H_{21} angle of this bond; a very weak hydrogen bond was observed at smaller (120–150°)

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(1) Brealey, G. J.; Kasha, M. *J. Am. Chem. Soc.* **1955**, *77*, 4462–4468.

(2) Pimentel, G. C. *J. Am. Chem. Soc.* **1957**, *79*, 3323–3326.

(3) Jaffé, H. H.; Orchin, M. "Theory and Applications of UV Spectroscopy"; Wiley: New York, 1962; p 187.

(4) Del Bene, J. *J. Am. Chem. Soc.* **1973**, *95*, 6517–6522.

(5) Iwata, S.; Morokuma, K. *J. Am. Chem. Soc.* **1973**, *95*, 7563–7575.

(6) Beecham, A. F.; Hurley, A. C. *Aust. J. Chem.* **1979**, *32*, 1643–1648.

(7) Beecham, A. F.; Hurley, A. C.; Johnson, C. H. J. *Aust. J. Chem.* **1980**, *33*, 699–705.

(8) Pulay, P. In "Applications of Molecular Electronic Structure Theory"; Schaefer, H. F., Ed.; Plenum: New York, 1977; pp 153–185.

(9) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823–2833.

(10) (a) Almlöf, J. University of Stockholm Institute of Physics Report 74-29, 1974. (b) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157–173. (c) Saebø, S. "MOLFORC—Program Description"; University of Oslo: Oslo, 1979. (d) Taylor, P. R., unpublished work.

(11) See, e.g.: Carsky, P.; Urban, M. "*Ab initio* Calculations"; Springer-Verlag: Berlin, 1980; pp 176–177.

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