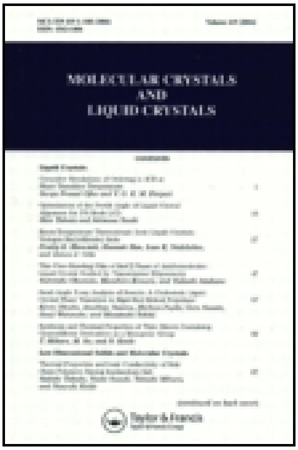

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Conformational Instability of Excited States of Symmetrical Molecules: Substituted Benzenes and Porphyrins

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Version of record first published: 21 Mar 2007.

To cite this article: J. H. Van Der Waals (1979): Conformational Instability of Excited States of Symmetrical Molecules: Substituted Benzenes and Porphyrins, Molecular Crystals and Liquid Crystals, 50:1, 301-304

To link to this article: http://dx.doi.org/10.1080/15421407908084438

Mol. Cryst. Liq. Cryst., 1979, Vol. 50, pp. 301–304

Printed in Holland

Conformational Instability of Excited States of Symmetrical Molecules:

Substituted Benzenes and Porphyrins

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(*Received June 16, 1978*)

Recent experimental material on the (pseudo-) Jahn-Teller instability of the lower excited states of some symmetrical π-electron systems will be reviewed. Two classes of compounds, representative of two distinct situations, are considered:

1) Benzene and some of its derivatives where the π-electron system of the parent molecule has a sixfold axis of symmetry and the Jahn-Teller instability arises from a doubly degenerate mode (e_{2g} in D_{6h}).

2) Metalporphins where a fourfold axis of symmetry is present and the Jahn-Teller instability arises via coupling by non-degenerate modes (b_{1g} or b_{2g} in D_{4h}).

THE METASTABLE TRIPLET STATE OF BENZENE AND SOME OF ITS DERIVATIVES

Since the pioneering theoretical work of Moffitt and Liehr[1] the problem of the geometry of benzene in its lowest triplet state has received considerable attention. The spectroscopic investigations of Burland, Castro and Robinson[2] have made it clear that strong vibronic coupling occurs which manifests itself, for instance, by a decrease of the $\nu_8(e_{2g})$ vibrational quantum from 1584 cm^{-1} in the ground state to 245 cm^{-1} in the $^3B_{1u}$ state. ESR and ENDOR experiments on the triplet state of C_6H_6 in a C_6D_6 host crystal[3] furnished unambiguous evidence that the hexagonal symmetry is broken: the electron spin distribution indicates a structure in which two opposite long bonds ("antiquinoid" form) occur. However, the low frequency of the ν_8 mode points to a "softness" of the electronic energy surface that acts as the potential for the ν_8 nuclear mode, and from a number of subsequent experiments it has appeared that the mean shape of the electron spin distribution is strongly affected by the environment and substituents.

Results will be reported obtained by Vergragt[4] and van Noort on three benzene derivatives in mixed crystals: toluene in benzene, *p*-xylene in *p*-xylene d_{10}, and aniline in *p*-xylene. The three systems have been studied by microwave induced delayed phosphorescence in zero field (MIDP), and the latter two also by conventional ESR on single crystals. It appears that all three molecules lower their symmetry on excitation into the triplet state. The twofold axis that passes through the substituent(s) in the ground state (when neglecting the internal structure of the NH_2 and CH_3 groups) is lost on excitation. This is borne out in a mutually consistent manner by the positions of the in-plane principal axes of the fine structure tensor (the "spin axes"), the spin density distribution over the aromatic CH groups, and the relative radiative decay rates of the upper two sublevels of the triplet state in zero field.

In Figure 1 the results for the *p*-xylene isotopically mixed crystal have been summarized by way of example. Particularly noteworthy is the large difference in spin density for the two pairs of CH groups, and the fact that the in-plane spin axes are rotated over an angle of 70° relative to their position in the C_6H_6 molecules in the C_6D_6 crystal.

At present, quantum chemical calculations are being undertaken to analyze what is going on. In a simple, intuitive picture it would seem that the molecules, like their parent compound, tend to distort to an antiquinoid form, but they do this in such a manner that the substituent group(s) end up in a terminal position of the allyl-like moieties which are separated by the two "long" bonds of the antiquinoid structure.

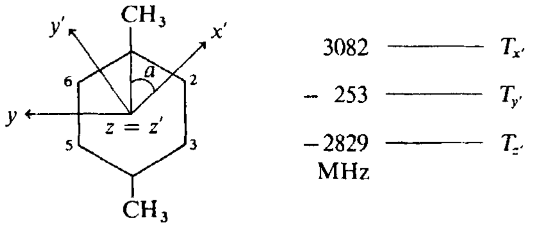

FIGURE 1 Zero-field splitting of the triplet state of *p*-xylene in an isotopically mixed crystal at 1.3 K. Direction of principal axes: $a = 68 \pm 1°$. Spin densities: $\rho_3 = \rho_6 = 0.29$; $\rho_2 = \rho_5 < 0.11$ Relative radiative decay rate in phosphorescence 0–0 band: $k^r_{x'}/k^r_{y'} = 0.4 \pm 0.1$.

PORPHINS IN *n*-ALKANE HOSTS

In recent years it has become clear that *n*-alkanes, such as *n*-octane and *n*-decane, constitute very suitable hosts for the study of the magnetic and optical properties of porphins (P). For sake of simplicity, let us restrict ourselves here to metalporphins with a diamagnetic ground state, of which MgP, ZnP, PdP are representative examples. Because of the fourfold symmetry of these molecules, one expects the lower excited states, singlets as well as triplets, to be orbitally degenerate. However, from a large number of optical and ESR experiments it has become clear that in the mixed crystals the degeneracy is lifted, with a crystal field splitting in the range of 10–100 cm^{-1}.

Continuing earlier work by Child, Hougen[5] has made a detailed study of the Jahn Teller instability for molecules with a fourfold axis of symmetry, in which case the coupling arises via (a) non-degenerate mode(s). It appears that the dynamical aspects of the problem are quite different from the more familiar situation where ternary axes of symmetry are present (cubical systems, benzene). Since the active nuclear mode now is one-dimensional in the space of the normal coordinates (and barring "accidental" degeneracies), the symmetrical conformation does not constitute a singular point on the electronic energy surface, but a simple intersection. Although the two sheets of the E_u electronic energy surface are shifted relative to each other and have minima for distorted conformations, there is no change in the vibrational frequencies, nor an interconversion of equivalent distorted forms via the active mode. For an isolated molecule the vibronic degeneracy would not be removed, but in an environment lacking a fourfold symmetry one of the orbital components is favoured over the other and this gives rise to the observed crystal field splitting of the two sets of vibronic levels.

To get an insight into the Jahn Teller coupling in porphyrins, the lower excited singlet (S_1) and triplet (T_0) states of MgP, ZnP and PdP are being studied by Zeeman spectroscopy and ESR in oriented single crystals of *n*-octane. From the data to be presented on the Zeeman studies of the $S_1 \leftarrow S_0$ absorption spectrum it appears that in the S_1 state of ZnP the Jahn Teller instability, though small energywise, has a pronounced effect on the spectral properties. By studying the Zeeman shifts of a number of vibronic lines Miss Jansen[6] established that the active mode has a frequency of 180 cm^{-1} and that the minima in the potential occur at a distance $\frac{1}{2}a = Q_0/\rho_0 = 0.55$ from the square form (Q_0 is the displacement along the active coordinate and ρ_0 the zero point amplitude of the active vibration). In a chemical sense one might, perhaps, conclude that on excitation of ZnP the central metal develops a tendency towards a two-coordination. For PdP, on the contrary, the Jahn Teller coupling in the state S_1 is negligible.

It is difficult to obtain information on the type of deformation that occurs on excitation into the singlet state S_1. However, by means of ESR experiments on metal porphins in *n*-alkane host crystals, one can get such information for the triplet state T_0. It has been found by Kooter[7] that the electronic structure of T_0 for MgP and ZnP is surprisingly similar to that of the free base, H_2P: the four methine groups (characterized by a high spin density) are equivalent, whereas the nitrogens occur in two inequivalent pairs.

Apparently, the dominant coupling is via a b_{1g} mode, causing the two orbital components to have symmetry planes through the nitrogen atoms.

The study of the Jahn Teller coupling represents only one aspect of our research on porphyrins. The ESR and Zeeman experiments have furnished a wealth of information on the electronic structure of their lower excited states. One aspect, closely linked to the Jahn Teller problem, is the orbital angular momentum in the state S_1. If $|x\rangle$ and $|y\rangle$ represent the two E_u orbital components as split by the crystal field (and in the absence of an external magnetic field) the orbital angular momentum is represented by the matrix element

$$\langle y|L_z|x\rangle = i\Lambda\hbar.$$

Miss Jansen[6] has found a value $\Lambda = 4.2 \pm 0.1$ for ZnP in the state S_1, which is in remarkably good agreement with the theoretical estimate of 4.35 obtained by McHugh *et al.*[8]

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