# Structure of the Short Wavelength Photoisomers of Bianthrone Analogues

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New unstable photoisomers absorbing at short wavelengths were observed for 10.10'-dimethyl-$\Delta^{9,9'}$-biacridanyl-idene, bithioxanthenylidene. bianthrylidene. and 10.10'-dihydroxybianthrylidene. A C_{2v} symmetry structure. considerably twisted about the four single bonds of the 9.9'-ethylene unit is suggested by a CFF–π electron–CI geometry calculation. This conclusion is supported by analyses of the low temperature n.m.r. spectra and of the effects of the conformational changes on the electronic transition energies. Complete thermal conversion to the starting isomer was observed in all cases.

Two different reversible photoisomerization modes have been thus far observed in bianthrone (Ia), bixanthenyl-idene (Ib), and their derivatives.[1-4] Photocyclization at

$$a; X = C{=}O$$
$$b; X = O$$
$$c; X = NCH_3$$
$$d; X = CH_2$$
$$e; X = CHOH$$
$$f; X = S$$

(I)
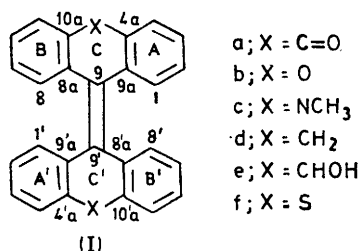
the 1 and 8' atoms produces the 4a,4b-dihydrophenan-threne-like [5] isomers C,[2,6] while the conformational photoisomers B (Figure 3f) are formed by torsion about

the 9,9' double bond in the fundamental (lowest energy) form denoted henceforth as A.

Torsion about the essentially double bond results in a red shift in the first absorption band from ca. 25 000 in A(Ia) to ca. 16 000 cm^{-1} in B. We now report a new type of conformational photoisomer observed for four analogues of bianthrone (Ic—f). As will be shown these unstable modifications (E forms, Figure 3c and d) are considerably twisted about the four essential 9a,9, 8a,9, 9'a,9', and 8'a,9' single bonds of the 9,9'-ethylene unit. This deformation results in a blue shift of the first electronic transition. The differences in the spatial arrangement of the four single bonds 9a,9, 8a,9, 9'a,9', and 8'a,9' in the A, B, and E forms may be visualized by a Newman projection along the 9,9'-bond (Scheme).

[1] R. Korenstein, K. A. Muszkat, and S. Sharafy-Ozeri, *J. Amer. Chem. Soc.*, 1973, **95**, 6177 and references cited therein.

[2] (a) R. Korenstein, K. A. Muszkat, and E. Fischer, *Helv. Chim. Acta*, 1970, **53**, 2101; (b) T. Bercovici, R. Korenstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, 1970, **24**, 531 and references cited therein.

[3] R. Korenstein, K. A. Muszkat, and E. Fischer, *Mol. Photochem.*, 1972, **3**, 379.

[4] R. Korenstein, K. A. Muszkat, and E. Fischer, *J. Photochem.*, 1976, **5**, 345, 447; *J.C.S. Perkin II*, 1976, in the press.

[5] K. A. Muszkat and E. Fischer, *J. Chem. Soc. (B)*, 1967, 662.

[6] G. Kortüm and H. Bach, *Z. Phys. Chem.*, 1965, **46**, 305.

As shown later (cf. Figure 3d and f) the two unstable modifications E and B owe their existence to the 1',8 and 1,8' steric repulsions which act as potential barriers to the E ⟶ A and B ⟶ A transformations.

SCHEME
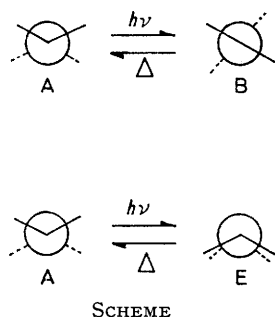
(a) *Experimental Results.*—Figure 1 (broken curve) shows the spectral changes produced by 313 nm irradiation of a propan-1-ol–propan-2-ol (3 : 2) solution of
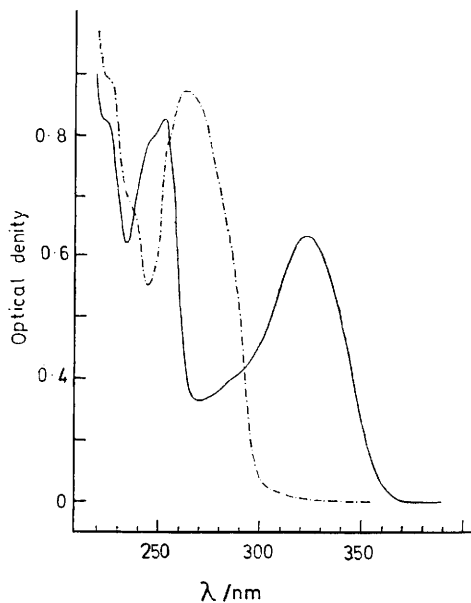

FIGURE 1 Full curve, absorption spectrum of A form of (Id); broken curve, absorption spectrum of E form of (Id) in propan-1-ol–propan-2-ol (3 : 2) at 113 K (both 4.5 × 10⁻⁵ M)

(Id) at 113 K. The first absorption band is shifted in this case from 31 000 [(Id), form A] to 37 700 cm⁻¹ in the E form. Similar changes were observed for (Ic, e, and f). Complete conversion A $\xrightarrow{h\nu}$ E has been obtained in every case, indicating the absence of the reverse photochemical processes E $\xrightarrow{h\nu}$ A. Both triplet energy sensitization and external spin–orbit coupling enhancement effects on the rate of the process A $\xrightarrow{h\nu}$ E indicate a triplet state process.[7]

The back thermal isomerization, E $\xrightarrow{\Delta}$ A, is quanti-

[7] R. Korenstein and K. A. Muszkat, ' Environmental Effects on Molecular Structure and Properties,' ed. B. Pullman, Reidel, Dordrecht, 1976, p. 561; R. Korenstein, K. A. Muszkat and E. Fischer, *Chem. Phys. Letters*, 1975, **36**, 509.

tative and monomolecular. The half-life times for this process are: (Ic), 15 s (223 K); (Id and e), 90 min (211 K); and (If), 22 min (268 K). Observed activation energy values range from 10 to 14 kcal mol⁻¹. The A $\xrightarrow{h\nu}$ E process is strictly monomolecular as shown by the following results. (1) The quantum yields of the A ⟶ E process in (Ic) (0.3 at 173 K in CS_2) and in (If) (0.01 at 213 K in 2-methyltetrahydrofuran) were not affected by increasing the concentrations from 4 × 10⁻⁵ to 4 × 10⁻⁴M. (2) The A ⟶ E process is only weakly (if at all) affected by large changes in the viscosity of the solvent. Thus in (Ie) (5 × 10⁻⁵M) in propan-1-ol–propan-2-ol (3 : 2) solutions, the A ⟶ E quantum yield decreases from 0.22 at 133 to 0.11 at 113 K, while the viscosity increases by a factor of 5 × 10³ (from 4 × 10⁴ at 133 K to 2 × 10⁸ poise at 113 K).[8]

The low temperature 90 MHz ¹H n.m.r. spectrum of the E photoisomer of (Ic) (Figure 2) was obtained by the technique previously developed for the B isomers.[1] Comparison of the spectra of the A form (full curve) and of the E form (broken curve) indicates that no valence isomerism is involved in the process A ⟶ E, as no new signals are observed in the spectrum of E in the region from δ 6.2 to 4.0. In the process A ⟶ E 1-, 8-, and 1'-, 8'-H signals are shifted downfield, from δ 6.58 to 7.84, the result of a deshielding effect.[1] This effect indicates[1] that process A ⟶ E involves the transfer of these protons from a region of highest shielding, in proximity

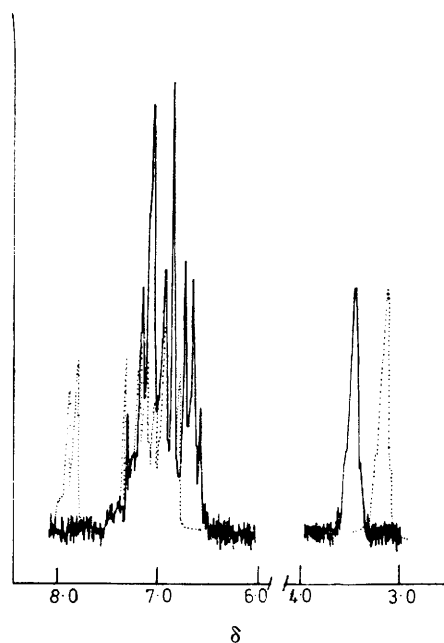FIGURE 2 Full curve, ¹H n.m.r. spectrum of A form of (Ic); broken curve, ¹H n.m.r. spectrum of E form of (Ic) in CD_2Cl_2–CS_2 (1 : 1) at 173 K (both 5 × 10⁻³M)

to the six-fold axis of the opposite benzene ring in A, to a region of lowest shielding close to the plane of the same

[8] J. S. Hutzler, R. J. Colton, and A. C. Ling, *J. Chem. and Eng. Data*, 1972, **17**, 324.

ring, in E. The quantitative aspects of this change are considered in section (c).

In the process A ⟶ E, the N-methyl protons are shifted upfield, from δ 3.47 to 3.21. Thus the aromatic 1-, 8-, 1'-, and 8'-protons on one hand and the N-methyl

(b) *Minimum Energy Conformations.*—The experimental data discussed thus far are obviously insufficient for a complete structure determination. In this respect the situation here is like that encountered previously with photoisomers B,[1] namely that the exact structure
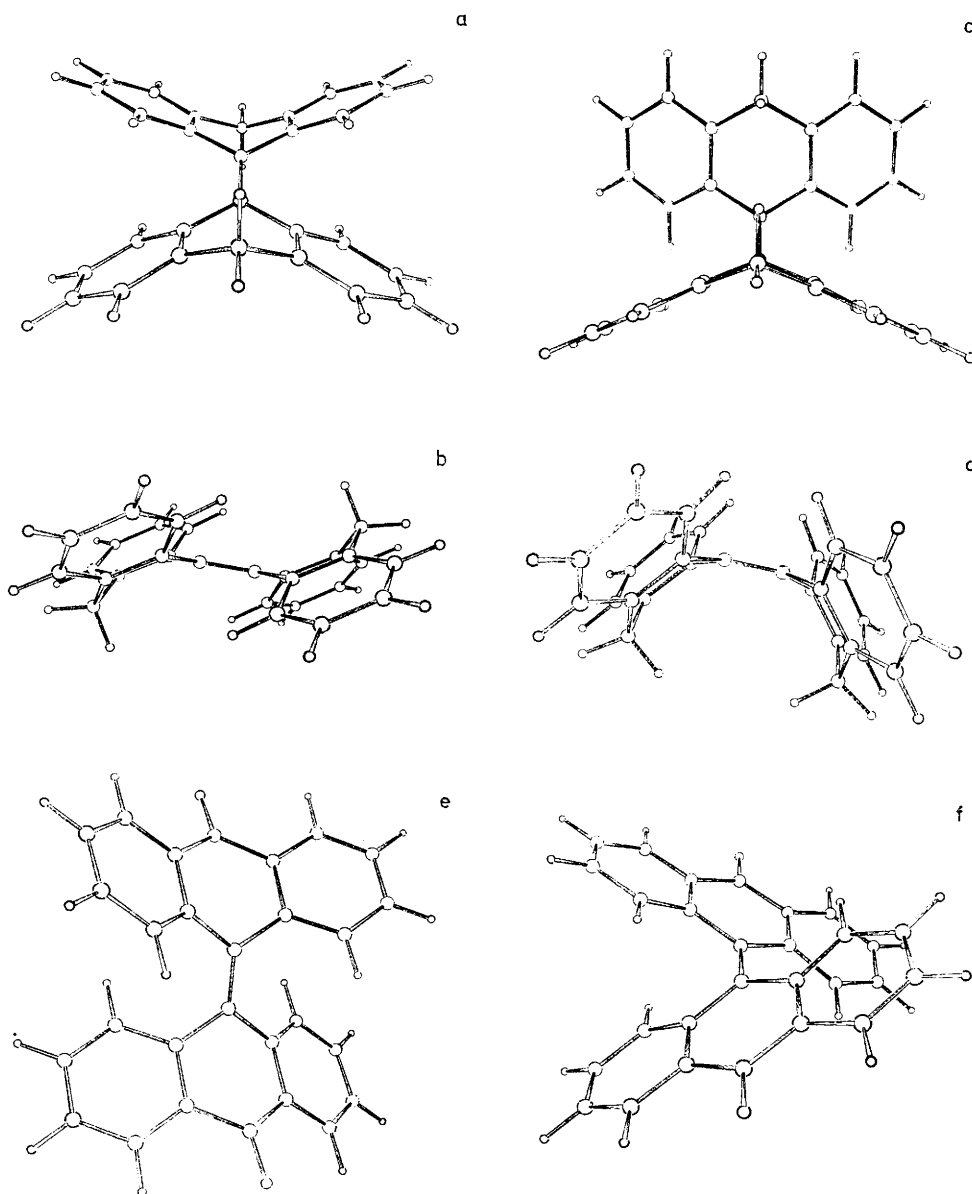

FIGURE 3 Calculated molecular conformations of A, E, and B forms: a, b, A form of (Id), front and side views; c, d, E form of (Id), front and side views; e, A form of (Ia); f, B form of (Ia)

protons on the other undergo opposite changes in diamagnetic shielding. According to the above interpretation this increase in diamagnetic shielding suggests that the N-methyl group is close to the plane of ring c in A, but farther removed from this plane in E. These two positions correspond to the equatorial (e) and axial (a) conformations indicated in Figure 3b. The N-methyl is thus equatorial in A, and axial in E.

of such unstable molecules as the photoisomers E can be obtained only by computation.

In order to establish the exact geometry of conformer E we have resorted to a search of the potential energy surface for a secondary minimum, in addition to that of the lowest energy form A. While in the previous study [1] only nonbonded and strain energy terms were included, the more refined Consistent Force Field-π-electron-CI

method of Warshel and Karplus [9] is used in the present work. In this approach the total electronic energy is composed of a π-electron contribution and of a σ core part based on a potential function method.

The method of Warshel and Karplus [9] uses efficient minimization procedures, and was shown to be suitable for obtaining the geometries of large nonplanar conjugated polyenes. Thus at least from the practical point of view this method is particularly well adapted for the present problem. For reasons of computational simplicity (Id) was chosen as a model. For comparison with the previous work [1] the structures of the A and B forms of bianthrone were recalculated by the present method. The calculated minimum energy cartesian co-ordinates of (Id) (A and E forms) and of (Ia) (A and B forms) are listed in Supplementary Publication No. SUP 21799 (5 pp.).*

The structures of (Ia) (A and B), shown in Figures 3e and f, are very similar to those inferred previously.[1] The structure of (Id)(A), shown in Figures 3a and b closely resembles that of (Ia)(A). Its symmetry is C_{2h}. In addition to this absolute minimum energy structure there is also a local minimum corresponding to isomer E. The initial co-ordinates for this form were obtained by twisting (Id)(A) by 180° about the 9,9'-double bond. The resulting optimized structure shown in Figures 3c and d, has C_{2v} symmetry. The calculated dihedral angles (τ) which differ considerably from either 0 or 180° are listed in Table 1. The torsion angles about

TABLE 1

Calculated dihedral angles (°) for nonplanar parts in (Ia)(A), (Ia)(B), (Id)(A), and (Id)(E)

		Dihedral angles			
Angle	Atoms	(Ia) (A)	(Ia) (B)	(Id) (A)	(Id) (E)
τ_a	1, 9a, 9, 9'	317	9	317	294
τ_b	9a, 9, 9', 9a'	2	230	180	201
τ_c	9a, 9, 9', 8a'	182	50	0	0
τ_d	4a, 9a, 9, 9'	139	182	144	121
τ_e	9a, 4a, X, 10a	21	2	42	43

the four central single bonds are larger in (Id)(E) than in (Id)(A). The values, reduced to the 0—$\pi/2$ range, are (Ia)(A), τ_a 43, τ_d 36; (Id)(E) τ_a 66, τ_d 59°. This difference in τ_a and τ_d (see below) is responsible for the blue shift of the first absorption band of E. The process A $\longrightarrow$ B in (Ia) also involves a large change in τ_a and τ_b (Table 1), though in the opposite direction than for process A $\longrightarrow$ E(Id). This change should contribute to the red shift of the first absorption band of B.

The calculated ground state energies of E(Id), B(Ia), as well as of the hypothetical E(Ia), relative to the energies of the A forms, are listed in Table 2.

As a particularly interesting outcome, our analysis provides a simple description of the relationship between the E and B photoisomers. Since the initial co-ordinates

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

for both isomers are obtained by torsion about the 9,9'-bond in the A form (*ca.* 50° for B, 180° for E), the potential surface of (Id) was also examined for a minimum corresponding to the B form. However, no stable local minimum could be found. This result agrees with the experimental data about the absence of B isomers

TABLE 2

Energies (kcal mol⁻¹) of E and B modifications of (Ia and d) relative to the A modification

	$E_B - E_A$	$E_E - E_A$
(Ia)	1.8 (5) [a]	16 [b]
(Id)		13

[a] Experimental value in parentheses.[1,2] [b] Hypothetic modification.

in (Ic—f). Qualitatively it is due either to a decrease in the 4a–X–10a bond angle from the trigonal value [*cf.* (Ia) *vs.* (Ic—e)] or to an increase in the X–4a and X–10a bond lengths [*cf.* (Ib) *vs.* (If)]. As a result rings c and c′ in (Ic—f) assume a boat conformation while those in (Ia) are more planar. This is shown by the τ_e values in Table 1, *e.g.* 21 in (Ia)(A), and 2° in (Ia)(B), compared with 42 in (Ia)(A) and 43° in (Id)(E).

Thus the H(1)–H(1′) and H(1)–H(8′), steric interactions are insufficient in the case of (Ic—f) for locking the molecule in a local minimum corresponding to an intermediate value of the torsion angle about the 9,9'-bond as in the B isomers. However, both in (Ia and b) these interactions are sufficiently large to supply the necessary energy barriers for trapping the B isomers in either ground or excited state conformations.

(c) *Analysis of the Deshielding Effect.*—The calculated atomic co-ordinates of (Id)(A) and (Id)(E) form the basis for a quantitative analysis of the deshielding effect on the 1-, 8-, 1′-, and 8′-protons of (Id) in the process A $\longrightarrow$ E. The diamagnetic shielding of these protons by the nearby benzene rings (*i.e.*, H-1 by ring b′, *etc.*) was calculated from the ring current model of Johnson and Bovey,[10] which was used also in the investigation of form B.[1] The diamagnetic shielding is a function of two geometric parameters. These are: ρ, the distance of the proton from the six-fold axis of the ring, and z, the distance between the proton and the plane of the ring. As all the shielding interactions of the type H-1–ring b′ are equal, we shall consider explicitly only this interaction in the following discussion.

The calculated parameters and shifts (Δ) for A (Id) and E (Id) are listed in Table 3. The ρ and z values for A and E support the qualitative interpretation of the deshielding effect in (Ic)(E) given in section (a). From the results of Table 3 it is seen that ring b′ exerts a moderate shielding effect (Δ^A 1.03 p.p.m.) on H-1 in the

[9] (a) A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, 1972, **15**, 5612; *Chem. Phys. Letters*, 1972, **17**, 7; *J. Amer. Chem. Soc.*, 1974, **96**, 5677; (b) A. Warshel and M. Levitt, Program QCFF/PI (QCPE No. 247), Quantum Chemistry Program Exchange.

[10] (a) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012; (b) F. A. Bovey, 'Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969, p. 64.

A form. However, in the E form the effect is changed to one of weak deshielding, Δ^E −0.35 p.p.m. The calculated difference is $\Delta_{calc} = \Delta^A - \Delta^E = 1.38$ p.p.m., in good agreement with the observed shielding difference, $\Delta_{obs} = 7.84 - 6.58 = 1.26$ p.p.m.

(d) *Effect of Torsion about Essential Single Bonds on Electronic Transition Energy.*—The change in electronic transition energy due to torsion about an essential [11]

TABLE 3

Diamagnetic shielding parameters of the 1-, 1'-, 8-, and 8'-protons in (Id)

	A	E
$\rho(Å)$	1.87	3.70
$z(Å)$	2.55	1.28
Δ_{calc}(p.p.m.)	1.03	−0.35

single bond in polyenes is most simply derived by applying first-order perturbation theory to the HMO one-electron energy expression.[12] A change $\delta\beta_{rs}$ in the
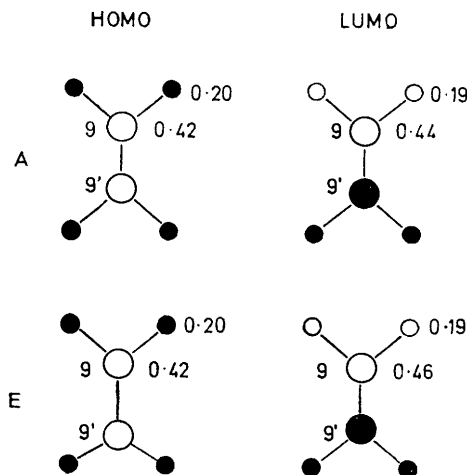

FIGURE 4 Highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) of A and E forms of (Id)

resonance integral β_{rs} between centres r and s results in a change $\delta\varepsilon_i$ in the one-electron energy ε_i, given by expression (1) where C_{ir} and C_{is} are the AO coefficients.

$$\delta\varepsilon_i = 2C_{ir}C_{is}\delta\beta_{rs} \tag{1}$$

We shall limit ourselves to the effect of deformations of the central ethylene unit on the first electronic transition. The present CI wave functions indicate that in the case of (Id) (A and E forms) the first transition is essentially a pure one-electron excitation from the highest

occupied MO (HOMO) to the lowest unoccupied MO (LUMO). These orbitals for both A and E forms of (Id) are shown in Figure 4. As these molecules are even alternants, the AO coefficients in the SCF wave functions for the occupied and unoccupied MOs (Figure 4) show an approximate mirror relationship.[12]

The transition energy change $\delta\Delta\varepsilon$ due to the torsion of N equivalent bonds is given by equation (2). Here l

$$\delta\Delta\varepsilon = 2N(C_{lr}C_{ls} - C_{kr}C_{ks})\delta\beta_{rs} \tag{2}$$

and k denote respectively the LUMO and HOMO, r is one of the 9 and 9' atoms and s one of the 9a, 8a, 9a', or 8a' atoms. In the present case ($N = 4$) considering the phases and coefficients of the MOs equation (2) may be approximated by (3). Assuming a dependence of

$$\delta\Delta\varepsilon \approx 16 \ C_{lr}C_{ls}\delta\beta_{rs} \tag{3}$$

β_{rs} on the torsional angle ϕ of the form (4) [12b] we obtain

$$\beta_{rs} = \beta_{rs}^0 \cos\phi \tag{4}$$

equation (5) for process A ⟶ E. C_{lr} and C_{ls} have

$$\delta\Delta\varepsilon \approx -16 \ \beta_{rs}^0 \sin\phi \ C_{lr}C_{ls} \ \delta\phi \tag{5}$$

the same sign (Figure 4) and β_{rs}^0 is negative. Thus for an increase in the torsional angle θ (positive $\delta\phi$), expression (5) indicates a *positive* $\delta\Delta\varepsilon$, *i.e.*, blue shift, as experimentally observed going from A to E.

The calculated τ_a and τ_d values in (Id)(A) and (Id)(E), as reported in section (b), were seen indeed to increase in this direction. The results of the full CFF–π–SCF–CI calculation support the above conclusions based on equation (5). Going from (Id)(A) to (Id)(E) shifts the calculated first singlet excitation energies from 32 880 to 36 660 cm⁻¹.

Figure 4 provides some indication about the mechanism of the (Id)(A) $\xrightarrow{h\nu}$ (Id)(E) process. A 'wagging' motion of the CH_2 group would result in such a conformational change but would involve severe transannular hydrogen–hydrogen interactions. These interactions would be avoided by a mechanism involving rotation about the 9,9'-bond, weakened in the excited state because of the transfer of an electron from a 9,9' bonding to a 9,9' antibonding MO.

[11] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.
[12] (*a*) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, **A191**, 39; (*b*) E. Heilbronner and H. Bock, ' Das HMO-Modell und seine Anwendung,' Verlag Chemie, Weinheim, 1968, ch. 6.