for carrying out the NOE experiments on the NIH sponsored Bruker WH-600 NMR.

Supplementary Material Available: ¹H NMR, IR, and high-resolution mass spectral data on all compounds and results of the NOE difference experiments (8 pages). Ordering information is given on any current masthead page.

Charge-Transfer-Biradical Excited States: Relation to Anomalous Fluorescence. "Negative" S_1–T_1 Splitting in Twisted Aminoborane

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We wish to report results of an ab initio calculation of the ground and excited states of aminoborane, H_2BNH_2, as a function of twist angle. At orthogonality, T_1 lies a little above S_1 and both are of charge-transfer-biradical nature. We believe that the results are useful for the understanding of anomalous fluorescence of the so-called twisted internal charge-transfer type.

Low-lying electronic states of two-electron two-orbital (A,B) systems are profitably discussed in terms of the four configurations, ^1AB, $^1A^2$, $^1B^2$, and ^3AB.[3] When A and B are orthogonal and A is at most moderately more electronegative than B, as in a twisted alkene, ^1AB and ^3AB represent the nearly degenerate S_0 and T_1 states, and $^1A^2$ with an admixture of $^1B^2$ represents the S_1 state (case I). If the electronegativity difference Δ increases sufficiently, $^1A^2$ becomes more stable than ^1AB and ^3AB. It then represents S_0, while the latter two describe the still nearly degenerate S_1 and T_1 states (case II).[4]
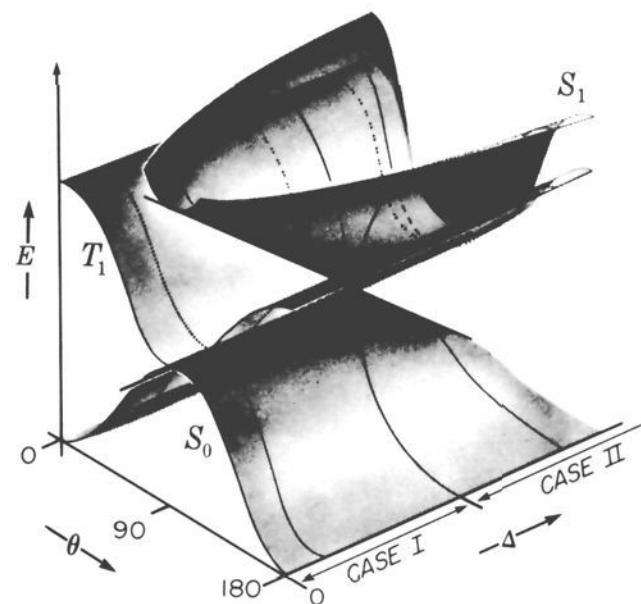
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(4) (a) Bonačić-Koutecký, V.; Köhler, J.; Michl, J. *Chem. Phys. Lett.* **1984**, *104*, 440. (b) In the first approximation (3 × 3 CI, $K_{AB} = 0$), the change from case I to case II occurs when the difference of the AO energies $\epsilon_B - \epsilon_A$ equals the Coulomb integral difference $J_{AA} - J_{AB}$. The existence of case I and case II situations, separated by a region of near or exact touching between the S_0 and S_1 surfaces, is not limited to twisted double bonds but is found more generally for molecules that can reach biradicaloid geometries, such as those capable of undergoing a ground-state forbidden pericyclic process. These considerations lead to prediction of the effect of polar perturbations on the shape of the S_1 surface and on the S_0–S_1 separation. The consequences for photochemical reactivity, in particular substituent effects and regiochemistry, will be reported elsewhere.

Figure 1. Schematic two-dimensional plot of S_0, S_1, and T_1 energies as function of the twist angle θ and electronegativity difference between two p orbitals at the termini of the double bond.
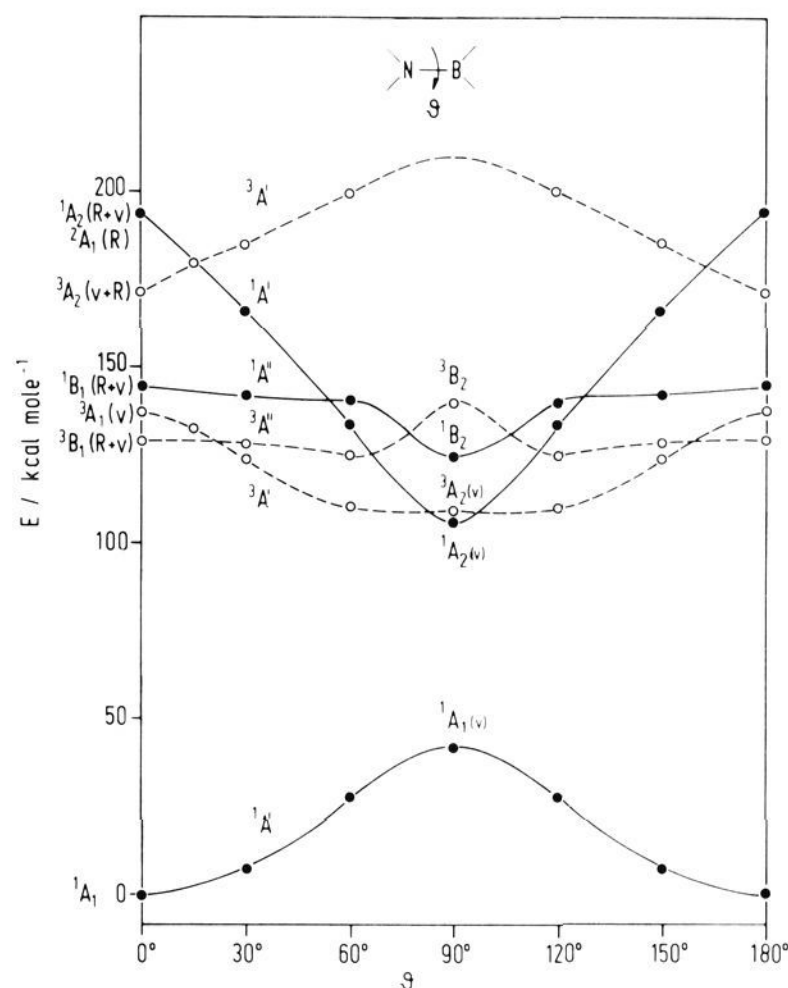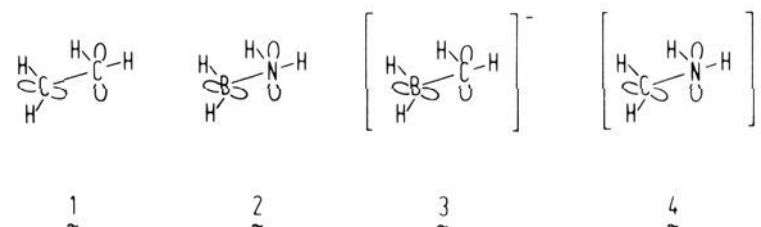

Figure 2. Energies of lowest singlet and triplet states of aminoborane as a function of twist angle θ around the B–N bond, obtained from the large scale MRD-CI treatments. Extrapolated energies for $T \to 0$ are plotted.

Three important situations are of interest: (i) ^1AB and ^3AB are nonpolar and $^1A^2$ zwitterionic (**1**), (ii) ^1AB and ^3AB are

zwitterionic and $^1A^2$ nonpolar (**2**), (iii) none of the three configurations involve charge separation (**3**, **4**). Since charge separation requires energy, situation i usually corresponds to case I and situation ii to case II, while situation iii lies at the border line between cases I and II, with S_0, S_1, and T_1 all nearly degenerate.[4]

S_1 and T_1 surfaces should have a minimum at an orthogonal geometry which is particularly unfavorable for S_0. Figure 1 plots the S_0, S_1, and T_1 energies as a function of the electronegativity difference Δ and the relative twist angle θ of two p orbitals located at the termini of a bond.

The situations i and iii have already been explored computationally in some detail.[4] Presently we deal with a prototype of the less well-documented situation ii, in which nearly degenerate S_1 and T_1 states are expected to be of "charge-transfer-biradical" nature and to lie high above the nonpolar S_0 state. Figure 2 shows the state energies of aminoborane calculated as a function of the twist angle θ by an ab initio method using a Dunning (3s, 2p, d, R) basis set[5] and the multireference CI[6] with about 10 000 configurations.

At planarity, several Rydberg states of aminoborane lie below the valence states. As θ increases, the state order changes in a manner familiar from calculations on alkenes.[7] At orthogonality, the lowest four states are of valence character. The wave functions of the S_0, S_1, and T_1 states are those expected from the above discussion: in S_0, $^1A^2$ enters with 92% weight; in S_1, ^1AB enters with 92% weight; in T_1, ^3AB enters with 92% weight. Thus, in S_0, the N atom carries a lone pair and the excitations into S_1 and T_1 involve a transfer of one of its electrons onto the B atom, producing charge-transfer-biradical states. Their calculated dipole moments are 4.8 D.

At orthogonality, where both S_1 and T_1 exhibit the expected minimum, S_1 actually lies a few kilocalories per mole below T_1. We are not aware of any other singlet ground state molecule for which such a "negative" S_1–T_1 splitting has been observed or calculated.

According to the simple four-configuration model outlined above, T_1 should lie below S_1 by a small amount ($2K_{AB}$). Introduction of additional CI preferrentially stabilizes S_1 and brings it below T_1. This is due to the "dynamic spin polarization" effect,[8] already well understood from the case of 90° twisted ethylene. Since this should be quite general, it is likely that a negative S_1–T_1 splitting will be found for other charge-transfer biradicals as well.

As far as we know, charge-transfer-biradical states of the type calculated here have not been observed for species as simple as our example, i.e., case II where A and B can each be well represented by a single AO. We believe that our calculations are sufficiently reliable for a prediction of photochemical events along the cis–trans isomerization path of aminoborane (in reality, other paths may be followed). After initial excitation of planar aminoborane into a S_1 or T_1 state of predominantly Rydberg nature, localized on the amino group, collisions should relax the molecule to orthogonal geometry where S_1 and T_1 are of charge-transfer-biradical nature and highly polar. Emission from the twisted state will have a large Stokes shift and will be quite sensitive to environmental effects.

Strongly Stokes-shifted emission from excited states of molecules twisted along a bond linking an acceptor to a donor has been reported in the gas phase,[9] nonpolar solvents,[10] and, above all, polar[11,12] solvents. These states are commonly referred to as "twisted internal charge transfer" (TICT) states.[13] In this sense,

at their orthogonal minima, the S_1 and T_1 states of aminoborane are TICT states, and its Rydberg states play a role analogous to that of the locally excited states of the usual TICT species, in which A and/or B reside on large conjugated moieties.

Aminoborane represents a particularly simple example of the TICT phenomenon and can be viewed as a prototype.[14] Not only does its simplicity permit an ab initio calculation with a high degree of reliability, it also offers clear insight into the physical origin of the preferred orthogonality of the A and B orbitals in the S_1 and T_1 states (cf. the previously empirical "minimum overlap rule"[11]).

(13) Since our model considerations do not demand that the orthogonality of A and B be reached by twisting, we view the concept of charge-transfer-biradical excited states as more general than the TICT concept. For instance, an aromatic radical cation linked by a saturated chain to an aromatic radical anion represents a charge-transfer-biradical excited state but not a TICT state. In this case, A is the HOMO of one and B the LUMO of the other aromatic moiety.

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Reaction of Cp₂Ti=CH₂ with Organic Halides: Evidence for a Radical Mechanism

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Metal carbenes have been demonstrated in such important catalytic processes as olefin metathesis[2] and Fischer–Tropsch CO[3] reduction and suggested as intermediates in Ziegler–Natta polymerization[4] and hydrocarbon cracking.[5] The reactivity patterns exhibited by isolated metal carbenes are divided into two classes—electrophilic carbenes I,[6] which add nucleophiles at the
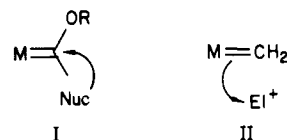
carbene carbon, and nucleophilic carbenes II,[7] which add elec-

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