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Enhancement of Through-Bond Coupling by Bond-Angle Distortion: Pyrazine

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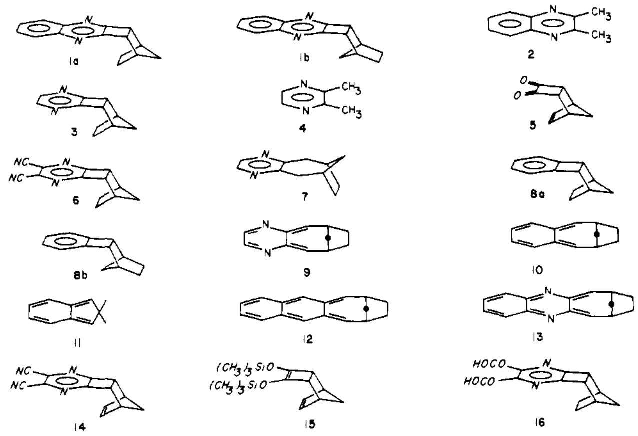
Abstract: The cyclobutapyrazine derivative, *endo*-3,4-pyrazinotricyclo[4.2.1.$0^{2,5}$]nonane (**3**), has been synthesized and subjected to a spectroscopic investigation. An inequivalence of the two faces of the pyrazine π system is revealed by the measured relative polarization directions of the $^1n\pi^*$ and $^1\pi\pi^*$ electronic transitions and is ascribed to a delocalization of the pyrazine orbitals into the low-symmetry saturated polycyclic system. A striking red shift of the $^1n\pi^*$ transition in **3** relative to 2,3-dimethylpyrazine and a similar shift of the n_+ ionization energy to lower values are ascribed to an enhanced through-bond coupling of the two nitrogen lone-pair orbitals due to distortion of bond angles at carbons 2 and 3 and to the resulting enhancement of the p character of the σ bond orbital through which the coupling occurs.

The relative energies of the lowest $n\pi^*$ and $\pi\pi^*$ transitions in the singlet and triplet manifolds are of considerable interest since they play an essential role in the photophysics of aza aromatics. It has been recently noted[2] that the singlet $n\pi^*$ transition in both the endo (**1a**) and the exo (**1b**) isomers of the cyclobutaquinoxaline **1** is remarkably red shifted with respect to the $n\pi^*$ transition in the unstrained model, 2,3-dimethylquinoxaline (**2**), while the differences in their singlet $\pi\pi^*$ transition energies are much smaller. It was suggested that this may be due to an increased energy of the n_+ orbital in **1** relative to **2**. However, a comparison of the photoelectron spectra of **1** and **2** did not provide conclusive evidence, because the n_+ ionization is masked by ionization from the top two occupied π orbitals in both compounds.

We now wish to report the synthesis of a cyclobutapyrazine, **3**, and an investigation of its spectroscopic properties in an effort to ascertain whether a similar shift relative to 2,3-dimethylpyrazine (**4**) is present and if so to elucidate its origin.

Chart I



Results

After some unsuccessful attempts at condensation of the dione **5** with ethylenediamine, moderate yields of the pyrazine **6** were ultimately obtained with 2,3-diaminomaleonitrile. The hydrolysis of the cyano groups in **6** and subsequent decarboxylation with copper in pyridine yielded the desired pyrazine **3** in low yield. In the decarboxylation step, a very small amount of a byproduct was isolated but could not be purified to better than about 85% purity, the rest being **3**. Its NMR, mass, and UV spectra suggest that this side product is the dihydro derivative **7**.

The UV absorption, fluorescence, and phosphorescence spectra and their polarization are shown in Figure 1 for **4** and in Figure 2 for **3**. The photoelectron spectra of **3** and **4** are compared in Figure 3 and the results of calculations are given in Figure 4.

Like **1a**, **1b**, and other benzocyclobutene derivatives such as the isocyclic analogues[3] **8a** and **8b**, **3** undergoes a photochemical transformation upon UV irradiation in a glassy solution at 77 K. By analogy to the previously investigated cases, we tentatively assign the product the *o*-quinodimethane structure **9**. This is supported by the close agreement of the observed UV excitation energies (Figure 5) with those of the isocyclic analogue **10** and with the results of semiempirical calculations.

Discussion

Spectral Assignments. The assignments of several low-energy electronic states of pyrazine are well established[4] and we assign the transitions in the very similar spectra presently observed for its dimethyl derivative, **4**, by analogy (Figure 1). The first absorption band at 31000–35000 cm^{-1} belongs to the singlet $n_+\pi^*$ transition, as does the very weak fluorescence. The purely electronic $n_+\pi^*$ transition moment is oriented perpendicular to the plane of the ring. The second absorption band, at 36000–41000 cm^{-1}, belongs to a singlet $\pi\pi^*$ transition analogous to the lowest $\pi\pi^*$ ($^1B_{2u}$) transition in benzene. It is polarized along the twofold symmetry axis (long in-plane axis) of **4**. The phosphorescence is assigned to the $^3n\pi^*$ transition and is polarized along the short in-plane axis of **4**. The lowest $^3\pi\pi^*$ state of **4** is presumably located in the vicinity of the 0–0 component of the $^1n\pi^*$ state, facilitating intersystem crossing.

These assignments are supported by the observed polarization degree[5] *P*. With excitation into the long-axis-polarized $\pi\pi^*$ band, *P* is negative near the origin of the fluorescence, as expected if

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(1) (a) University of Utah. (b) IBM Research Laboratory.

(2) R. P. Steiner, R. D. Miller, H. J. Dewey, and J. Michl, *J. Am. Chem. Soc.*, **101**, 1820 (1979).

(3) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510 (1976).

(4) For assignments of the $n_+ \rightarrow \pi^*_{-1}$ ($^1B_{3u}$), $\pi_1 \rightarrow \pi^*_{-1}$ ($^1B_{2u}$), and $\pi_2 \rightarrow \pi^*_{-1}$ ($^1B_{1u}$) transitions, see, e.g.: K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectrosc.*, **22**, 125 (1967); M. N. Pisanias, L. G. Christophorou, J. G. Carter, and D. L. McCorkle, *J. Chem. Phys.*, **58**, 2110 (1973); W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 2034 (1975); R. W. Wagner, P. Hochmann, and M. A. El-Bayoumi, *J. Mol. Spectrosc.*, **54**, 167 (1975). For a discussion of the vibronic structure of the $n_+ \rightarrow \pi^*_{-1}$ transition see G. Orlandi and G. Marconi, *Chem. Phys. Lett.*, **53**, 61 (1978), and references therein. For assignment of the $n_- \rightarrow \pi^*_{-1}$ ($^1B_{2g}$) transition see G. Snatzke and G. Hajos in "Excited States in Organic Chemistry and Biochemistry", B. Pullman and N. Goldblum, Eds., D Reidel Publishing Co., Dordrecht, Holland, 1977, p 295. For the assignment of the photoelectron spectrum see R. Gleiter, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **55**, 255 (1972).

(5) F. Dörr in "Creation and Detection of the Excited State", Vol. 1, Part A, A. A. Lamola, Ed., Marcel Dekker, Inc., New York, 1971, p 53.

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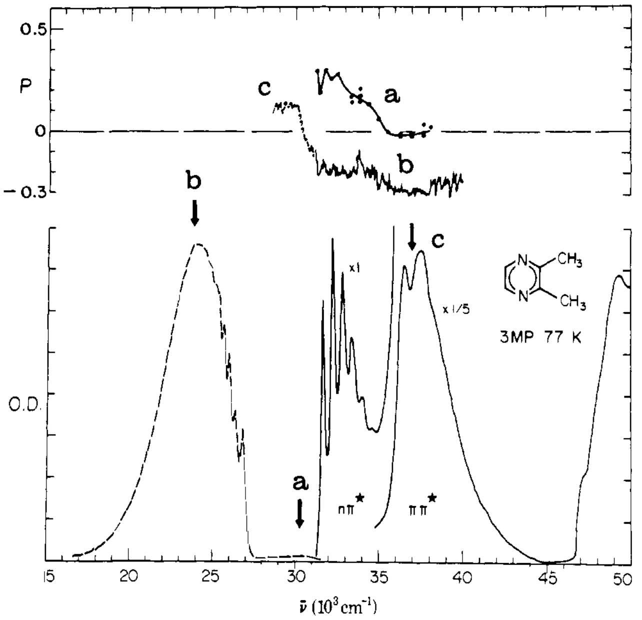

Figure 1. Spectra of 2,3-dimethylpyrazine (**4**) at 77 K in 3-methylpentane glass. Full line: absorption; dashed line: emission. The polarization degree *P* is given at the top (arrows indicate the excitation and monitoring energies). Curve a: polarization of fluorescence monitored at arrow a. curve b: polarization of phosphorescence monitored at arrow b. Curve c: polarization of emission excited at arrow c.

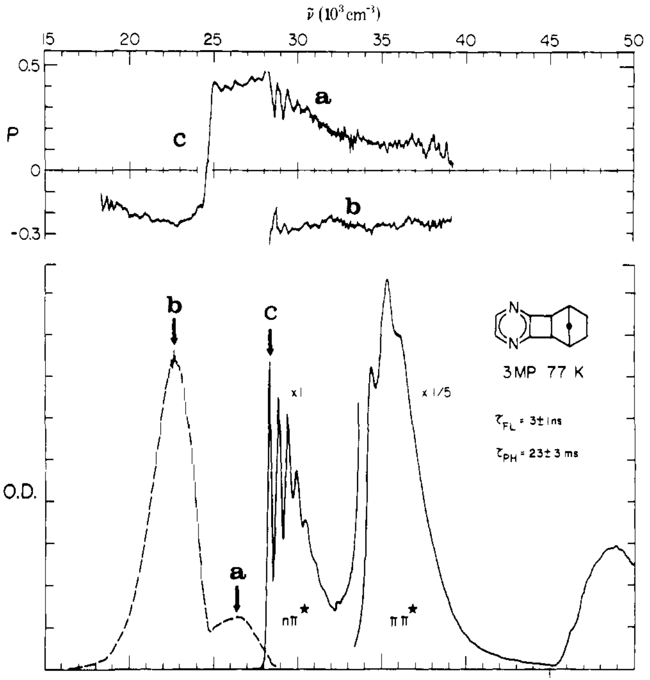

Figure 2. Spectra of *endo*-3,4-pyrazinotricyclo$[4.2.1.0^{2,5}]$nonane (**3**). See caption to Figure 1.

the latter is out-of-plane polarized. As one proceeds toward the maximum of the fluorescence, *P* changes rapidly and becomes clearly positive. This indicates that much of the fluorescent intensity is vibronically induced and has borrowed a long-axis-polarization direction. Given the weakness of this emission and our detection limits, we have not been able to resolve the individual vibronic peaks. The same factor forced us to record the polarized fluorescence excitation spectra at the maximum of the fluorescence rather than its origin, and it is hardly surprising that the theoretical limits for *P* are not reached. In the region of the $\pi\pi^*$ band, *P* is about zero rather than $-{}^1/_3$, and in the region of the $n\pi^*$ band, it is about 0.3 rather than ${}^1/_2$. On the other hand, in the phosphorescence polarization spectrum, *P* is nearly exactly at the

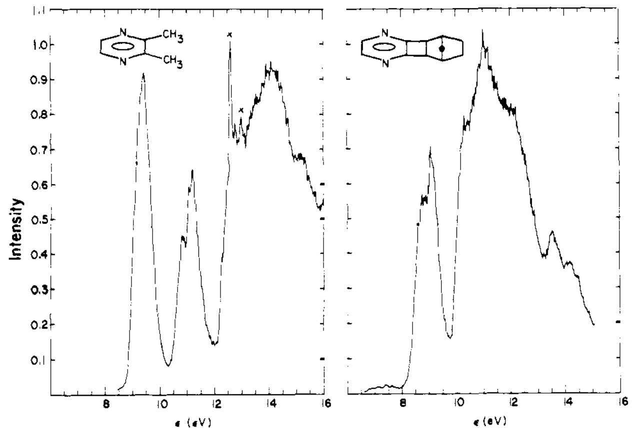

Figure 3. He I photoelectron spectra of **3** and **4**. The crosses indicate Xe calibration lines.

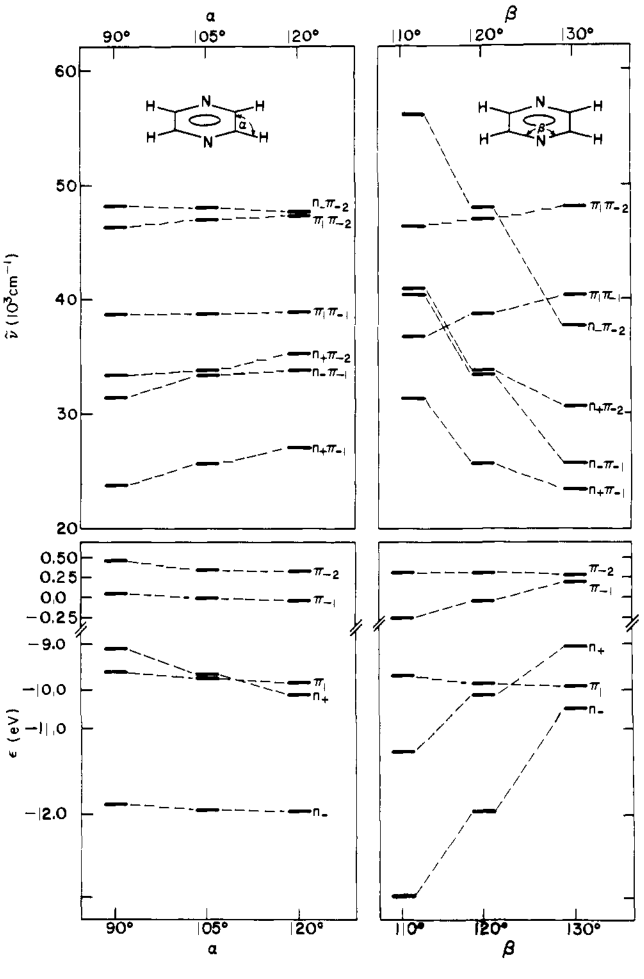

Figure 4. Orbital energies (bottom) and excitation energies (top) of pyrazine as a function of geometrical distortion, calculated by the INDO/S method.

theoretical limit $-{}^1/_3$ in the region of the long-axis-polarized ${}^1\pi\pi^*$ absorption, as expected if the ${}^3n\pi^*$ phosphorescence is purely short-axis polarized. In the region of the ${}^1n\pi^*$ absorption, the value of *P* is only about −0.2, indicating that the vibronic mixing in the ${}^1n\pi^*$ state provides also a certain degree of short-axis-polarized intensity. This appears to be particularly noticeable in the valleys between the main peaks of the $n\pi^*$ band, where *P* is less negative, and fits in with the fine structure in the plot of *P* for fluorescence excitation, which was less positive in these same regions.

The spectra of the cyclobutene **3** (Figure 2) are so similar to those of **4** that there can be no doubt about the assignment of the

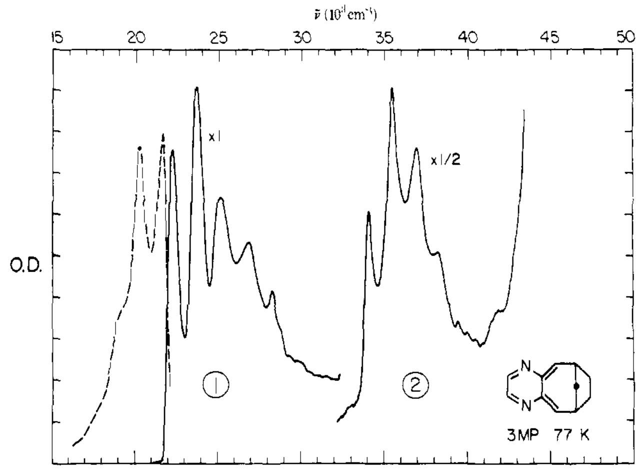

Figure 5. Spectra of 3,4-pyrazinobicyclo[4.2.1]nona-2,4-diene (**9**). See caption to Figure 1.

^{1}nπ^* and $^1\pi\pi^*$ bands in absorption, the ^{1}nπ^* fluorescence, and the ^{3}nπ^* phosphorescence. The polarization curves again support the assignment. They show that vibronic borrowing plays a less important role in **3** than it did in **4**, and they further display a point which has recently been of some interest:[6] in conjugated systems which possess a plane of local symmetry but are contained in a molecule which lacks a plane of overall symmetry, the σ–π separation is not strictly valid and the two faces of the "π system" are inequivalent.

Inequivalence of the Two Faces of a π System. In a conjugated system such as **3**, whose two faces are not equivalent by symmetry, one must in principle expect the inequivalence to be reflected in physical properties as well as reactivity. Reactivity differences could be of both a trivial nature, due to differential steric hindrance of the two faces, or a more subtle nature, due to electronic (hyperconjugation or polar) effects, which could operate at some distance. Evidence for such nontrivial differentiation of the two faces has been reported recently.[6]

In **3**, the inequivalence of the two faces is primarily due to having benzylic C–H bonds on one side and benzylic C–C bonds on the other. This should cause an unsymmetrical delocalization of π, π^*, and n orbitals involved in electronic transitions into the saturated part of the molecule, and if this delocalization is large enough, it should be detectable through its effect on polarization directions. The symmetry of **3** demands that transitions be polarized either along the N–N axis ("short in-plane axis") or perpendicular to it, along a direction which lies in the molecular plane of symmetry. If delocalizing interactions with the saturated part of the molecule which breaks the plane of π symmetry were negligible and the two π faces equivalent, the two directions perpendicular to the N–N axis which are allowed in **4** would still be the only permissible ones: perpendicular to the plane of the pyrazine ring or parallel to it. If the two faces are effectively inequivalent, any polarization direction in the plane perpendicular to the N–N axis is permitted.

These considerations suggest that polarized spectroscopy should provide a very sensitive probe for distinguishing the electronic inequivalence of the two faces of a π system and it is interesting to examine our results for **3** in this light (Figure 2). We first note that the ^{3}nπ^* phosphorescence, polarized along the N–N axis, should be perpendicular to both the ^{1}nπ^* and the $^1\pi\pi^*$ absorption, regardless of whether the two faces are equivalent or not. Indeed, the polarization degree *P* of phosphorescence excitation has very nearly the theoretical value $-^1/_3$ throughout the absorption region, with no significant difference between the ^{1}nπ^* and $^1\pi\pi^*$ transitions. The only deviation is a decrease of the negative magnitude of *P* in the valleys between the peaks of the ^{1}nπ^* band, similar to that already noticed in the case of **4**, and undoubtedly of the same vibronic origin. The polarization degree *P* of the emission observed upon excitation into the 0–0 peak of the ^{1}nπ^* band is near the expected values $+^1/_2$ and $-^1/_3$ for the ^{1}nπ^* fluorescence and the ^{3}nπ^* phosphorescence, respectively, with small slopes indicating a small amount of vibronic mixing. In contrast to **4**, the fluorescence of **3** is stronger and not much perturbed by vibronic borrowing, so that the exact wavelength of monitoring the polarization degree of fluorescence excitation has little effect. In the region of the ^{1}nπ^* band, *P* nearly reaches the theoretical limit of $+^1/_2$ at the peaks but is noticeably less positive in the valleys between them. This supports the above postulate of vibronically induced intensity polarized along the N–N axis of the ^{1}nπ^* absorption.

Table I. Calculated Electronic Transitions in 3[a]

transition	energy, cm^{-1}	dominant config	osc. strength	polarization[b]
1	26 100	$n_+ \rightarrow \pi^*_{-1}$	0.017	66° out-of-plane[c]
2	32 500	$n_+ \rightarrow \pi^*_{-2}$	0.008	N-N axis
3	36 100	$\pi_1 \rightarrow \pi^*_{-1}$	0.17	long in-plane axis
4	37 900	$n_- \rightarrow \pi^*_{-1}$	0.000	
5	44 300	$\pi_1 \rightarrow \pi^*_{-2}$	0.27	N-N axis

[a] Results of INDO/S calculations obtained for a geometry optimized by MINDO/3. Only transitions below 50 000 cm^{-1} are listed. [b] "Plane" refers to the plane of the pyrazine ring. [c] Perpendicular to the N-N axis, tilted away from the norbornane moiety.

Table II. Excitation Energies of Band Origins (cm^{-1})[a]

	3	4
$^1\pi\pi^*$	34 400	36 500
^{1}nπ^*	28 300	31 600
^{3}nπ^*	24 500	27 000

[a] The positions of the origins were estimated from spectra given in Figures 1 and 2.

The striking result in Figure 2 is the value of *P* for fluorescence excitation in the region of the $^1\pi\pi^*$ transition. If the ^{1}nπ^* fluorescence and the $^1\pi\pi^*$ absorption were polarized perpendicular to each other, the value should be $-^1/_3$. The observed value is +0.12 even more positive than in **4** in which the fluorescence was strongly vibronically mixed while in **3** it is not. The high value of *P* cannot be blamed on experimental artifacts such as depolarization since values very near the theoretical limits are observed elsewhere in the spectrum. Rather, we take it to mean that the two transitions, although both polarized perpendicular to the N–N axis, are not polarized perpendicular to each other. The standard formula,[5] $\cos^2 \alpha = (3P + 1)/(3 - P)$, yields an angle of 47° between the two polarization directions. The actual angle is probably somewhat larger since the theoretical limits, $+^1/_2$ and $-^1/_3$, are not exactly reached elsewhere in the spectrum.

This result provides direct evidence for the lack of equivalence of the two faces of the pyrazine π system in **3** due to electronic effects. It does not indicate whether only one or both of the transitions deviate from the direction which they would have in the absence of interaction with the saturated part of the molecule (out-of-plane of the pyrazine ring for ^{1}nπ^*, long-axis in-plane of the pyrazine ring for $^1\pi\pi^*$). In order to investigate this further, we have performed calculations by the INDO/S method.[7] The results are summarized in Table I. They suggest that the transition moment direction of the $^1\pi\pi^*$ transition is hardly perturbed at all by the symmetry-breaking saturated part of the molecule, but rather that it is the ^{1}nπ^* transition which is no longer polarized exactly perpendicular to the pyrazine ring but at an angle of only 66° to it, tilted away from the norbornane moiety. Qualitatively, it is reasonable that the transition-moment direction of the ^{1}nπ^* transition should be more easily perturbed, since this transition is weaker. Also, the n_+ orbital is known to be delocalized well beyond the two nitrogen atoms. Insofar as the calculations

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(6) L. A. Paquette, R. V. C. Carr, M. C. Böhm, and R. Gleiter, *J. Am. Chem. Soc.*, **102**, 1186 (1980).

(7) M. Zerner and J. Ridley, *Theor. Chim. Acta*, **32**, 111 (1973).

are correct, the differentiation of the two faces of the π system of **3** is due to an asymmetrical delocalization of its n electrons than its π electrons.

Transition-Energy and Orbital-Energy Differences between 3 and 4. The ${}^1n\pi^*$, ${}^1\pi\pi^*$, and ${}^3n\pi^*$ transitions of **3** are shifted to lower energies relative to those of **4** by about 3300, 2100, and 2500 cm^{-1}, respectively (Figures 1 and 2 and Table II, measured for 0–0 transitions). These are significant shifts considering the seemingly minor nature of the perturbation and cause the separation between the ${}^1\pi\pi^*$ and ${}^1n\pi^*$ levels to increase by about 1000 cm^{-1} upon going from **4** to **3**. The large shift of the ${}^1n\pi^*$ transition appears to be associated specifically with the presence of a fused four-membered ring. For instance, it is absent in **7**, whose ${}^1n\pi^*$ transition has a 0–0 peak at 31 300 cm^{-1}. A similar preferential stabilization of the ${}^1n\pi^*$ level has been observed[2] for **1a** and **1b** and it is of interest to ask whether it is due to a destabilization of the n_+ orbital.

This question is best addressed by using photoelectron spectroscopy and relying on Koopmans' theorem. Figure 3 provides a comparison of the results for **3** and **4**. Judging by peak intensities and comparison with pyrazine, we conclude that the intense first peak of **4** observed at 9.41 eV corresponds to two superimposed ionizations, due to the n_+ and the π_1 orbitals. In **3**, this peak is doubled, with a pronounced shoulder at 8.75 eV and a maximum at 9.05 eV. It appears that the n_+ orbital is shifted by ca. 5300 cm^{-1} and the π_1 orbital by ca. 2900 cm^{-1} to higher energies, demonstrating that the UV spectral shifts can be accounted for qualitatively in terms of orbital-energy shifts.

In summary, then, it would appear that a fusion of a cyclobutene ring to the 2,3 positions of pyrazine, as in **3**, or quinoxaline, as in **1**, causes a remarkable increase in the energy of the n_+ orbital and a similar decrease in the ${}^1n\pi^*$ excitation energy and it is quite likely that the effect is general. The changes in the π_1 orbital energy and the ${}^1\pi\pi^*$ excitation energy are in the same direction but smaller. The increased ${}^1n\pi^*-{}^1\pi\pi^*$ splitting in the cyclobutene derivative **3** may be responsible for its greatly increased yield of fluorescence since the ${}^1n\pi^*$ level may lie well below the ${}^3\pi\pi^*$ level in **3** while they are close in energy in pyrazine itself and in **4**.

The Origin of Orbital-Energy Shifts. Enhancement of Through-Bond Coupling by Ring Fusion. Our original suspicion[2] that the increase in the energy of the n_+ orbital in **1** or **3** is due to additional coupling of the lone pairs through the benzylic C–C bond in the four-membered ring has not been confirmed by INDO/S[7] calculations, as there seems to be little delocalization of the lone pairs into this relatively distant bond.

We now propose that the striking shifts of the n_+ energy is a novel manifestation of the "rehybridization effect" due to the geometric distortion of valence angles at carbons 2 and 3 attendant upon the fusion of the four-membered ring onto an aromatic ring.[8,9] Such a distortion will change the two outside C⋯C—C angles, with values of approximately 120°, into two unequal C⋯C—C angles, one of which is nearly 90° and the other nearly 150°, as is demonstrated most dramatically by the X-ray structure of [1,2:4,5]dicyclobutabenzene.[10] The original nearly exactly sp^2 hybridization will then change: the hybrid orbitals pointing in directions approximately 90° apart will have an increased p character; the third hybrid, exocyclic to the four-membered ring, will have an increased s character and increased electronegativity. This increase of electronegativity has been used to account for a variety of properties of benzocyclobutenes and related compounds,[8,9] such as the increased acidity of hydrogens in position 1 of biphenylene and the decreased basicity of 2,3-cycyobutapyridine (proton affinity[11] = 223.3 kcal/mol) relative to 2,3-dimethylpyridine (proton affinity[11] = 226.2 kcal/mol).

While the chemical consequences of the increased electronegativity of the one hybrid orbital are now well-known, those of the increased p character of the other two hybrid orbitals apparently have not been observed. We propose that the increase in the p character of the orbitals which form the σ bond between carbons 2 and 3 is responsible for more effective through-bond coupling between the two lone-pair orbitals on the nitrogen atoms and in this fashion is a major contributor to the increase in the energy of the n_+ orbital. According to Hoffmann,[12] the energy of the n_+ orbital is increased above that of the primitive lone-pair n orbitals by interaction with the 2–3 σ bond, and this interaction will be stronger if the energy of the 2–3 σ-bond orbital increases and is brought closer to that of the n orbitals by an increase of the p character in the two hybrid orbitals involved.

The effect is undoubtedly at least partially compensated by two factors. One is a decrease of the energy of the lone-pair n orbitals due to the inductive effect of the neighboring carbon; the other is a secondary geometrical change caused by the ring fusion. This is a decrease of the C–N–C angles,[9,10] which will increase the s character of the lone-pair n orbitals on nitrogen. It is remarkable that a strong shift of the n_+ orbital to higher energies still results.

These qualitative considerations are fully supported by our INDO/S[7] calculations of orbital energies and excitation energies, which produce just the expected trends (Figure 4). The great sensitivity of the calculated $n\pi^*$ energies to the bond angles assumed in the calculation makes it difficult to predict the excitation energies of **3** and **4** in the absence of structural information and we have not included such results in Figures 1 and 2. A calculation of the equilibrium geometry by the MINDO/3 method, followed by an INDO/S calculation of the excitation energies, produced results which were in only fair agreement with experiment (shifts in the correct direction, but too small) and we suspect that the calculated valence angles were not correct.

The shift of the π_1 orital to higher energies and the decrease in the ${}^1\pi\pi^*$ excitation energy upon going from **4** to **3** can be accounted for in a way similar to that used to rationalize such shifts in hydrocarbons[13] and do not require further comment here.

The Diaza-*o*-quinodimethane 9. While a detailed investigation of the chemistry and spectroscopy of the photoproduct **9** will require a considerable amount of additional work, it is already possible to present its absorption and fluorescence spectra (Figure 5). They are sufficiently similar in position and vibrational structure to those of the isocyclic analogue[3] **10** to reassure us that the photochemical reactions of **8** and **3** are indeed analogous and the structure assignment correct, but they also show some differences.

First, the diaza replacement red shifts the first observed $\pi\pi^*$ transition by ca. 2000 cm^{-1}. It also shifts the second observed $\pi\pi^*$ transition by an amount which is harder to determine since its location is difficult to discern in **10**. Second, while in **10** the first $\pi\pi^*$ transition is much more intense than the second observed one, in **9** the intensities are comparable and the second one is actually the more intense.

The red shift and the difference in intensities are in perfect agreement with the results of our INDO/S and PPP calculations. Although $n\pi^*$ transitions are undoubtedly present, they are most likely hidden under $\pi\pi^*$ absorption. The difference in intensities can also be understood in qualitative terms: while the first $\pi\pi^*$ transition is into a "plus" excited state in Pariser's classification[14] for alternant hydrocarbons, the second observed $\pi\pi^*$ transition is into a "minus" excited state and thus forbidden as long as alternant symmetry is present. The diaza replacement, which removes alternant symmetry, makes both transitions allowed in a manner analogous to the well-known cases of naphthalene vs. quinoxaline, anthracene vs. phenazine, etc. In the isoindene **11**, where alternant symmetry is only weakly removed by hypercon-

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(8) R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965); A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).

(9) R. P. Thummel, *Acc. Chem. Res.*, **13**, 70 (1980), and references therein.

(10) J. L. Lawrence and S. G. G. MacDonald, *Acta Crystallogr., Sect. B.*, **B25**, 978 (1969).

(11) D. H. Aue, K. N. Houk, and R. P. Thummel, private communication.

(12) R. Hoffman, *Acc. Chem. Res.*, **4**, 1 (1971).

(13) C. Santiago, R. W. Gandour, K. N. Houk, W. Nutakul, W. E. Cravey, and R. P. Thummel, *J. Am. Chem. Soc.*, **100**, 3730 (1978); F. Brogli, E. Giovannini, E. Heilbronner, and R. Schurter, *Chem. Ber.*, **106**, 961 (1973).

(14) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956); J. Koutecky, *ibid.*, **47**, 1501 (1967).

jugation in the five-membered ring, the second observed $\pi\pi^*$ transition is already distinct, if still quite weak.[15]

Calculations with extensive configuration interaction predict a transition into a doubly excited $\pi,\pi \rightarrow \pi^*\pi^*$ state between the two observed $\pi\pi^*$ transitions. It should be very weak and there is no evidence for it in the absorption spectra of **9**, **10**, or **11**, although some indication for its presence is provided by the polarization of the fluorescence of **11**.[15] The calculations which correctly reproduce the red shift of the first $\pi\pi^*$ transition upon going from **10** to **9** predict that the energy of the transition into the doubly excited state should be affected much less. This is completely analogous to the situation in the naphthoquinodimethanes **12** and **13**, where some experimental confirmation of these theoretical results is available.[2]

A more thorough understanding of the electronic excited states of **9**, **10**, and the biradicaloid quinodimethane molecules in general would be highly desirable but will require an additional experimental effort.

Experimental Section

***endo*-5′,6′-Dicyano-3,4-pyrazinotricyclo[4.2.1.0^{2,5}]non-7-ene (14).** The bromination of *endo*-3,4-bis(trimethylsiloxy)tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**15**) (15 mmol) was performed as previously described.[2] After the mixture was dried for 2 h at 0 °C over magnesium sulfate, the carbon tetrachloride was removed on the rotary evaporator and the orange residue immediately dissolved in 15 mL of glacial acetic acid. This solution was added rapidly to a solution containing 1.78 g (16.5 mmol) of diaminomaleonitrile (DAMN) in 35 mL of acetic acid at 100 °C. The heating was continued for 13 h. After the reaction mixture was cooled to 0 °C, 200 mL of ether and 150 mL of water was added and the acid neutralized with solid potassium carbonate. The resulting precipitate was filtered and washed with ether, and the combined ether extracts were dried over magnesum sulfate. Removal of the ether yielded 1.2 g of a solid brown residue. This solid was recrystallized from a minimum of ether to yield ultimately 700 mg of product (mp 145–47 °C). Sublimation at 110 °C (0.02 mm) yielded completely colorless material. ^{1}H NMR (CDCl$_3$) δ 1.91 (br d, J = 9 Hz, 1 H), 2.15 (br d, J = 9 Hz, 1 H), 3.38 (m, 2 H), 4.28 (m, 2 H) and 5.75 (t, J = 2 Hz, 2 H); UV (EtOH) λ_{max} 347 (1178), 290 (8009), and 245 nm (6478); mass spectroscopic mol wt 220.0723, for $C_{13}H_8N_4$ calcd mol wt 220.0748. Anal. Calcd for $C_{13}H_8N_4$: C, 70.90; H, 3.66; H, 25.44. Found C, 70.22; H, 3.74; N, 25.15.

***endo*-5′,6′-Dicyano-3,4-pyrazinotricyclo[4.2.1.0^{2,5}]nonane (6).** Pd/C (70 mg, 5%) was stirred with 8 mL of ether and equilibrated with hydrogen from a gas balloon. At this point a solution of 300 mg (1.36 mmol) of **14** in 15 mL of ether was injected and the hydrogenation was continued for 2 h at 25 °C. The catalyst was then filtered and washed with ether. When the ether was concentrated and cooled to −15 °C, the product **6** precipitated: 250 mg; mp 155–156 °C; ^{1}H NMR (CDCl$_3$) δ 0.85 (m, 2 H), 1.62 (m, 2 H), 2.87 (m, 2 H), and 4.15 (m, 2 H); UV (EtOH) λ_{max} 342 (1314), 297 (8762), 290 (8981), and 243 nm (8214); mass spectroscopic mol wt 222.0905, for $C_{13}H_{10}N_4$ calcd mol wt 222.0885. Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.25; H, 4.54; N, 25.21. Found C, 70.06; H, 4.57; N, 25.31.

***endo*-5′,6′-Dicarboxy-3,4-pyrazinotricyclo[4.2.1.0^{2,5}]nonane (16).** To a suspension of 1.570 g (7 mmol) of **6** in 200 mL of water was added 16.5 g (300 mmol) of sodium peroxide in portions over 0.5 h. The mixture was then heated in a bath (105 °C) for 6.5 h. The yellow solution was cooled to 25 °C and the pH adjusted to 4.5 with 6 N nitric acid. At this point, a solution of 5.1 g of silver nitrate in 50 mL of water was added and the precipitate collected by centrifugation. The air-dried solid was suspended in 10 mL of water and 13 mL of 1.2 N HCl was added. After vigorous stirring the precipitated silver chloride was removed by filtration. The solid was washed with water, air dried, and extracted two times with 50 mL of hot acetone. The aqueous filtrate was evaporated to dryness and the residue extracted with acetone. The combined acetone extracts were evaporated on the rotary evaporator. The residue was triturated with ~10 mL of CH$_2$Cl$_2$ (residue dissolved then reprecipitated) and the solid removed by centrifugation to yield 603 mg of the desired diacid (39%): mp 161–163 °C dec; ^{1}H NMR (acetone-d_6) δ 0.82 (m, 2 H), 1.51 (m, 2 H), 1.90 (m, 2 H), 2.65 (br s, 2 H), and 4.01 (m, 2 H). Anal. Calcd for $C_{13}H_{14}N_2O_5$ (monohydrate): C, 56.02; H, 4.34; N, 10.07. Found: C, 55.52; H, 4.49; N, 9.84.

***endo*-3,4-Pyrazinotricyclo[4.2.1.0^{2,5}]nonane (3).** A solution of 693 mg (1 mmol) of the diacid **16** in 7 mL of dry pyridine was placed in a Pyrex tube with 173 mg of copper powder. The solution was degassed and sealed under argon and heated to 195 °C for 2.5 h. The tube was then cooled, opened, and diluted with ether. All solids were removed by centrifugation and the solvent evaporated under vacuum to yield 80 mg of a greenish solid. TLC (silica gel, 85:15 hexane–ethyl acetate) examination of this material indicated predominantly a single compound with a small amount of a material of similar but slightly lower R_f. The major product was isolated by preparative TLC (85:15 hexane–ethyl acetate) and collected by GLC (10% SE-30, glass, 6 ft × 0.25 in, 140 °C) to yield ~45 mg of the desired pyrazine: mp 89–90 °C; ^{1}H NMR (CDCl$_3$) δ 0.86 (dd, J = 8, 2 Hz, 2 H), 1.45 (d, J = 8 Hz, 2 H), 1.80 (d, J = 10 Hz, 1 H), 1.89 (d, J = 10 Hz, 1 H), 2.67 (br s, 2 H), 3.94 (br s, 2 H), 8.25 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 26.1, 38.7, 45.2, 55.5, 144.2, 163.8; mass spectroscopic mol wt 172.0971, for $C_{11}H_{12}N_2$ calcd mol wt 172.0999; UV (3-methylpentane) λ_{max} 353 (1200), 346 (1428), 338 (1486), 334 (1286), 288 (14143), 282 (23429), and 275 nm (sh, 20571).

The minor product was enriched to ~85% during the TLC separation. At this point the only detectable contaminant was the pyrazine **3**. The difficult nature of the separation coupled with the small sample size precluded further purification. Examination of the spectral data of the enriched sample led to a tentative assignment of 3,4-pyrazinobicyclo-[4.2.1]nonane (**7**) as the structure of the byproduct. ^{1}H NMR (CDCl$_3$) δ 1.06 (dd, J = 8, 1.5 Hz, 2 H), 1.73 (m, 3 H), 2.07 (m, 1 H), 2.61 (d, J = 7 Hz, 2 H), 2.99 (d, J = 16 Hz, 2 H), 3.21 (ddd, J = 16, 7, 1.5 Hz, 2 H), 8.30 (s, 2 H); UV (3-methylpentane) λ_{max} 319, 314, 308, 302 nm; mass spectroscopic mol wt 174.1152, for $C_{11}N_{14}N_2$ calcd mol wt 174.1156.

Measurements. The solvent purification procedure and the instrumentation used for the measurement of low-temp. UV–vis absorption and emission spectra as well as fluorescence and phosphorescence polarization and lifetimes have been described elsewhere.[16] In each measurement, a fresh GLC-purified sample of **3** was used. The photoconversion to **9** was accomplished with use of a 200W Hg lamp equipped with a 280 nm cut-off filter and a Corning 7-54 UV-transmitting visible-absorbing filter. The NMR spectra were recorded on a Varian HA100 or SC-300 instrument and the chemical shifts were recorded on a Varian 731 spectrometer.

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