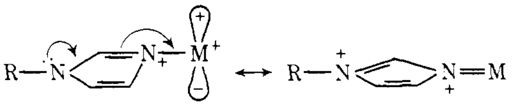
leaving a pentacoordinate Fe^{II} compound, **2d**, curve 2. The rest of the spectra in Figure 4 clearly show that this pentacoordinate iron, which reversibly binds carbon monoxide, is neither oxygenated nor oxidized by oxygen. The film of **1a** was prepared by the same procedure as for the "open film" of **2c** and its ability to bind oxygen has been reported previously.[8a]

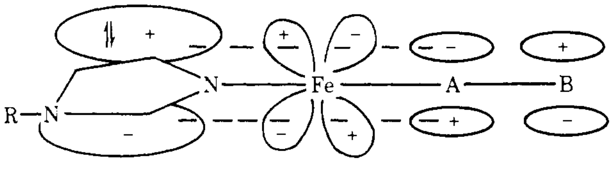
Thus, both the pyridine film **2d** and the imidazole film **1a** bound CO reversibly and both films were stable indefinitely toward oxidation by 1 atm of oxygen.[15] However, the pyridine compound **2d** in such a film showed no tendency to bind oxygen whereas the film of **1a** bound oxygen just as it did at $-45°$ in methylene chloride[8b] or as a pure solid compound.[8a] These results imply that the factors influencing oxidation and binding are not necessarily the same. Having prepared a simple, stable heme-oxygen complex, we can now study these factors in detail.

The fact that our compound **1a** binds oxygen and carbon monoxide almost as strongly as does myoglobin tells us that the neighboring group effect plus the basic nature of imidazole are the most important attributes of the myoglobin protein.

Although **1a** and **2a** have similar affinities for CO, they differ by at least 3800 in affinity for O_2. A possible explanation of the extraordinary differentiation between O_2 and CO by the imidazole compound might be in the π basicity (sideways basicity) of imidazole as discussed by Wang for hemes[3a] and described more generally elsewhere.[16]



We suggest, in addition, that it is the unusually large π basicity of imidazole compared to other π bases serving to make the iron back-bond more strongly with the empty electronegative π^* orbitals of oxygen, which is important.



This π back-bonding to AB becomes more important as the σ basicity of the ligand AB decreases and the π electronegativity of AB increases. Since the σ basicity (protic basicity) decreases in the order $CO > O_2$, we might expect O_2 to depend more strongly upon the π basicity of the proximal base than does CO. This, rather than a solvent effect, is probably responsible for the difference in selectivity between NO and CO displayed by myoglobin and by the piperidine-heme complexes reported recently.[17-19]

However, there is an important solvent effect on oxidation rates which we will discuss separately.

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[15] These results are reminiscent of the results reported for another model by J. H. Wang, *J. Amer. Chem. Soc.*, **80**, 3168 (1958).

[16] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1958, pp 183-185.

[17] D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 4087 (1973), and references given therein.

[18] Our results could also explain the instability of the pyridine-Fe^{II}-O_2 complex recently reported by Baldwin and Huff[19] although it is difficult to compare their nonheme iron complex with iron porphyrins.

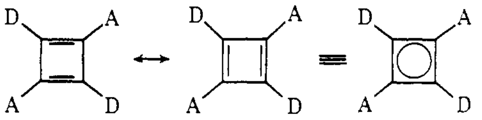
[19] J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, **95**, 5757 (1973).

Rapid Double Bond Shift in a Donor-Acceptor Substituted Cyclobutadiene. Evidence from 584-Å and X-Ray Photoelectron Spectroscopy

Sir:

In contrast to cyclobutadiene, whose fleeting existence has thus far precluded a determination of its ground-state geometry and spin multiplicity, donor-acceptor substituted cyclobutadienes[1] are perfectly stable molecules whose chemistry is now well established.[2] The available data regarding their structure are considerably more varied.

Both the observed equivalence of the $N-CH_2$ proton nmr signals down to $-46°$ (for $A = COOC_2H_5$, $D = N(C_2H_5)_2$) and HMO calculations, which yield identical π bond orders within the four-membered ring, point to the resonance hybrid shown below.



1

A recently published X-ray structure analysis for **1** appears to substantiate this formulation in that all ring CC bond lengths were found to be equal.[3]

However, the poor agreement factor reported in this study ($R = 0.12$) leaves doubts as to the correctness of the proposed structure. These doubts are reinforced by the anomalous uv spectrum[4] of **1**; the long wavelength transition, observable over a span of 8000 cm^{-1} (λ_{max} 25,500 cm^{-1}, ϵ_{max} 2.37), is strongly nonvertical, indicating that the ground- and first excited-state potential surfaces are markedly different. Since **1** is formally a nonbenzenoid hydrocarbon, it is tempting to attribute this disparity to the effect of double bond fixation operating in the ground state. MINDO/2 calculations by Weiss and Murrell[5] support this view and indicate a low barrier for the interconversion of the energetically equivalent valence tautomers.

In order to throw light on these apparently inconsistent results, the 584-Å and X-ray photoelectron spectra of **1** have been measured and compared with those of the

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[1] R. Gompper and G. Seybold, *Angew. Chem., Int. Ed. Engl.*, **7**, 824 (1968); M. Neuenschwander and A. Niederhauser, *Helv. Chim. Acta*, **53**, 519 (1970).

[2] R. Gompper and G. Seybold in "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," E. D. Bergmann and B. Pullman, Ed., The Israel Academy of Sciences and Humanities, Jerusalem, 1971, p 215; R. Gompper and G. Seybold in "Topics in Nonbenzenoid Aromatic Chemistry," in press.

[3] H. J. Lindner and B. v. Gross, *Angew. Chem., Int. Ed. Engl.*, **10**, 490 (1971). Professor Lindner has informed us that further refinement is in progress and will soon be published.

[4] G. Seybold, Ph.D. Thesis, Universität München, 1969.

[5] R. Weiss and J. N. Murrell, *Tetrahedron*, **27**, 2877 (1971).

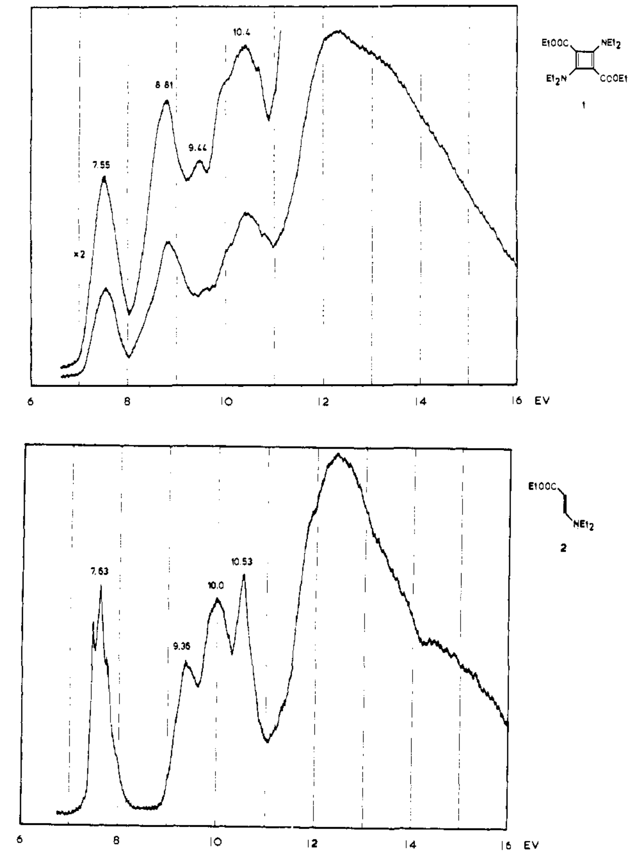


Figure 1.

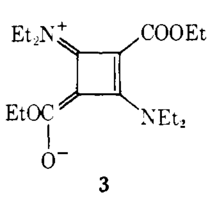
pertinent model,[6] β-diethylaminoethyl acrylate, **2** (Perkin-Elmer PS-18 and AEI ES-100 electron spectrometers, respectively). The relevant findings are as follows.

(a) The C_{1s}, N_{1s}, and O_{1s} electron spectra of **1** and **2** are on the whole very similar, both in shape and abolute binding energies (*cf.* Table I). There is evidence from the C_{1s} spectra for three different types of carbon atoms, with the carbonyl C_{1s} ionizations coming at highest binding energy. The other C_{1s} levels are too close in energy so that no attempt was made to deduce their ordering from the spectra. The N_{1s} peak is in both molecules considerably sharper than the O_{1s} peak, and there is a trend to higher binding energy, on going from **2** to **1**. At first sight this seems to indicate that zwitterionic structures such as **3** or **4** contribute to the ground state of **1**. However, the fact that the O_{1s} peak in **1** is shifted to higher rather than lower binding energies, quickly eliminates this possibility. Moreover, the N_{1s} shift of 0.8 eV is quite small, considering for example the 3.5 eV difference in the N_{1s} binding energies[7] of NH_3 (398.8 eV, solid) and NH_4NO_3 (402.3 eV). Note that the N_{1s} binding energies of NH_3 and **2** are identical within experimental error; this militates against zwitterionic structures contributing to the ground state of **2** as well.

Table I. C_{1s}, N_{1s}, and O_{1s} Core Level Binding Energies in eV for **1** and **2**

	C_{1s}			N_{1s}	O_{1s}
1	285.0 ± 0.25	286.5[a] ± 0.5	289.0 ± 0.25	399.6 ± 0.25	531.5 ± 0.5
2	285.0 ± 0.25	285.8 ± 0.5	288.5 ± 0.25	398.8 ± 0.25	531.0 ± 0.5

[a] Shoulder.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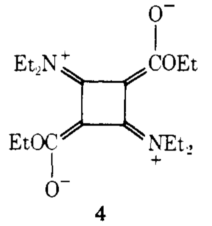
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(b) Both 584-Å photoelectron spectra show (Figure 1) the expected low-energy π band whose maximum (7.55 eV in **1**, 7.63 eV in **2**) is found at trivially lower energies in the case of **1**. The resonance integral[8] of the newly formed π bonds (on going from **2** to **1**) is thus only a fraction of that which one usually meets with in fully delocalized aromatic π systems.[9] This observation is clearly incompatible with a square cyclobutadiene structure and can only be explained on the basis of localized double bonds linked through essential single bonds.

(c) The first band in the 584-Å spectrum of **2** is sharp, with a full width at half maximum intensity (fwhm) of 0.40 eV, and consists of a short vibrational progression in about 1300 cm^{-1}, likely the C=C stretching mode. On passing to **1**, the vibrational structure is blurred, and the fwhm increases to 0.68 eV, thereby providing complementary evidence for the conclusion drawn from the broad Franck–Condon envelope of the first uv transition.

(d) In accord with the singlet nature of **1** there is no evidence for an exchange splitting in any of the higher 584-Å photoelectron bands.

In summary, the ground state of **1** is most economically described in terms of two essentially unperturbed, weakly interacting aminoacryl ester moieties, whereas the first excited singlet and the ground state of the cation are likely to be fully delocalized. It is therefore tempting to conclude that the apparent discrepancy in the interpretation of the nmr and X-ray findings, on the one hand, and of the uv and pe data, on the other hand,

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(6) 2 exists exclusively in the trans form. Inasmuch as the cis and trans isomers differ only in the long-range interaction between the nitrogen lone-pair AO and the carbonyl π orbital, little difference in the energy of the highest occupied π level is expected. This is fully confirmed by the identical first IP's of the isomeric dicyanoethylenes (H. Bock and H. Stafast, *Chem. Ber.*, **105**, 1158 (1972)) and various enol ethers (H. Mayr and W. Schmidt, unpublished).

(7) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

(8) Assuming the resulting π level splitting to be symmetrical, the resonance integral of the new π bonds is given by the difference in the vertical first IP's of 1 and 2. This assumption, however, is rather a rule than a law, *i.e.*, the actual resonance integral may be larger. Complicating features in 1 include (a) mixing with unoccupied levels, leading to a lowering of the mean energy of the two π levels, (b) reorientation of the wave functions due to the effect of the substituents, and (c) rehybridization at the ring carbon atoms, caused by a tilting of the sterically overlapping substituents out of the ring plane. An assessment of the importance of these effects will have to await a more complete analysis of the 584-Å photoelectron spectrum than given here.

(9) The π resonance integral in fully conjugated aromatic hydrocarbons has been determined to be −3.0 ± 0.2 eV from photoelectron spectroscopy; *cf.* R. Boschi, J. N. Murrell, and W. Schmidt, *Discuss. Faraday Soc.*, **54**, 116 (1972).

are the result of a double bond shift which is fast on the time scale of the nmr and X-ray experiment. Providing the barrier for this process is not appreciably higher than kT, both structural models—a square, fully delocalized, and a rectangular, rapidly interconverting species—would yield delusively similar electron density maps. In order to choose between these alternatives, accurate temperature factors obtained at sufficiently low temperature would be mandatory.

We conclude that donor–acceptor substituted cyclobutadienes such as **1** owe their remarkable stability not so much to the intervention of zwitterionic structures but to strong second-order bond fixation[10] in the dynamic sense, an inference which is fully in accord with the analysis given in ref 5. There are indications that the bond distortion in **1** is comparable to, or even greater, than that encountered in biphenylene whose coannular bonds have a length of 1.51 Å.[11] The 584-Å photoelectron spectrum of this molecule[12] shows peaks at 7.61, 8.90, 9.68, and 10.08 eV which correlate with the benzene e_{1g} band at 9.24 eV. Using a crude first-order perturbation argument, the coannular π resonance integral is estimated from these data to be -1.2 eV, *i.e.*, even larger than that deduced for **1** from the difference in the first IP's of **1** and **2**.

Acknowledgment. One of the authors (W. S.) wishes to thank Mr. H. J. Lempka and Perkin-Elmer Ltd. (Beaconsfield, U. K.) for their hospitality and the opportunity to obtain the 584-Å photoelectron spectra.

[10] For terminology, see G. Binsch and E. Heilbronner in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, p 815.

[11] J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, **20**, 87 (1966).

[12] Photoelectron spectra of nonbenzenoid hydrocarbons, including biphenylene, have been discussed by W. Schmidt, Conference on The Photoelectron Spectroscopy of Molecules, The Chemical Society, Brighton, Sept 1972.

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Properties of the [4]Annulene System. Induced Paramagnetic Ring Current

Sir:

Recent remarkable achievements in annulene[1] chemistry are, undoubtedly, the spectral characterization of [4]annulene (cyclobutadiene) (**1**) detained in a matrix at low temperatures[2–6] and the isolation of its derivatives in a pure state.[7] We have extensively examined (or reexamined) several approaches toward the construction of this reactive system and have unexpectedly found that a classical ring-expansion method *via* Δ^2-cyclopropenylmethylene does indeed proceed remarkably well with highly substituted precursors. We wish to record herein physical and chemical properties of methyl tri-*tert*-butyl[4]annulenecarboxylate (**2**) and tri-*tert*-butyl[4]annulene (**3**), in comparison with those of **1**. Compound **3** is of particular significance in that it represents the first demonstration of the chemical shift of a proton (protons) directly attached to the [4]-annulene ring, and thus provides important information concerning the induced ring current of the cyclic 4π-electron system.[8]

Reaction of methyl lithiodiazoacetate[9] with tri-*tert*-butylcyclopropenium fluoroborate[10] in a 1:1 mixture of diethyl ether and tetrahydrofuran at $-110°$ provided a yellow crystalline adduct (**4**) in 88% yield. Photolysis of **4** in oxygen-free pentane at $-78°$ proceeded smoothly, and when a *ca.* 1 *M* solution was irradiated, there formed, toward the cessation of nitrogen evolution, a large amount of crystalline precipitate, which was recrystallized from pentane ($-80°$) to afford light brown needles (**2**).[11] The yield is estimated to be more than 90% and **2** readily sublimes at 50° (0.01 mm) despite its molecular weight of 278.4. Spectral data of **2** as shown in Table I are clearly consistent with the formulation of the [4]annulene system for this compound and the nmr spectra show the presence of four olefinic carbons and C_{2v} (but not C_{3v}) symmetry in **2**. Chemical reactions of **2** further support the above structural assignment. Thus, addition of 1.2 equiv of maleic anhydride to a pentane solution of **2** at $-30°$ led to the quantitative formation of an adduct, which is formulated as **5**, but not as a dihydrobenzvalene derivative.[12] Although the absorptions of the two olefinic carbons appear in a somewhat lower region than normally expected,[13] the (chemical shift) values compare very well with those of tri-*tert*-butylcyclobutene (**6**) (see Table I). As expected,[14] the pmr (and cmr) spectra of

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[1] This term is defined by F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.*, **84**, 260 (1962).

[2] C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); A. Krantz, C. Y. Lin, and M. D. Newton, *J. Amer. Chem. Soc.*, **95**, 2744 (1973).

[3] S. Masamune, M. Suda, H. Ona, and L. M. Leichter, *J. Chem. Soc., Chem. Commun.*, 1268 (1972).

[4] G. Maier and B. Hoppe, *Tetrahedron Lett.*, 861 (1973). Alkyl substituted **1** was generated in a matrix earlier: G. Maier and M. Schneider, *Angew. Chem., Int. Ed. Engl.*, **10**, 809 (1971); G. Maier, G Fritschi, and B. Hoppe, *ibid.*, **9**, 529 (1970).

[5] O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Amer. Chem. Soc.*, **95**, 614 (1973); O. L. Chapman, D. De La Cruz, R. Roth, and J. Pacansky, *ibid.*, **95**, 1337 (1973).

[6] The lifetime of 1 in the gas phase was determined: (a) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967); (b) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, **91**, 1875 (1969).

[7] (a) H. Kimling and A. Krebs, *Angew. Chem., Int. Ed. Engl.*, 11, 932 (1972); (b) R. Gompper and G. Seybold., *ibid.*, 7, 824 (1968).

[8] Because of the intrinsic nature, cmr absorptions are relatively insensitive to ring current effects, even if carbons are uniquely positioned in the system to detect them. Obviously, signals due to the annular carbons provide virtually no information about the effects. See A. V. Kemp-Jones, A. J. Jones, M. Sakai, C. P. Beeman, and S. Masamune, *Can. J. Chem.*, **51**, 767 (1973); H. Günther, H. Schmickler, H. Konigshoten, K. Recker, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **12**, 243 (1973). V. Boekelheide, private communication, May 3, 1973.

[9] U. Schöllkopf and H. Frasnelli, *Angew. Chem., Int. Ed. Engl.*, **9**, 301 (1970); Recent review: M. Regitz, *Synthesis*, 351 (1972).

[10] J. Ciabattoni and E. C. Nathan, III, *J. Amer. Chem. Soc.*, **91**, 4766 (1969); J. Ciabattoni, E. C. Nathan, III, A. E. Feiring, and P. J. Kocienski, *Org. Syn.*, in press.

[11] Compounds **2** and **3**, as obvious from the test, are extremely reactive toward oxygen, and all operation involving these species was performed either in a vacuum system or drybox, using argon as an inert gas.

[12] For the chemical behavior of 1,3-di-*tert*-butyl[4]annulene, see P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969).

[13] G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, Chapter 3; J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972, Chapter 3.

[14] Restricted rotation along the axis of $C(sp^3)–C(sp^3)$ single bond was first observed by J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967), and reviewed by H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970). The isolation of rotational isomers was recently achieved by M. Ōki and G. Yamamoto, *Chemistry Lett.*, 45 (1972). Also see M. Ōki and O. Yamamoto, *Tetrahedron Lett.*, 727 (1973), and references quoted therein.