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GROUND STATES OF CONJUGATED MOLECULES—XXI*

BENZOFURANS AND BENZOPYRROLES†

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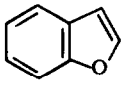
Abstract—Calculations are reported for several benzo derivatives of furan and indole, using the semi-empirical SCF MO Π approximation developed in these laboratories. These indicate that isobenzofuran and isoindole should be much less stable, and have lower ionization potentials, than benzofuran or indole.

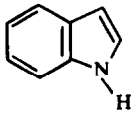
INTRODUCTION

AN INTERESTING problem in heteroaromatic chemistry is provided by a comparison of the "normal" heteroaromatic compounds benzofuran (I) and indole (II) with the isoconjugate isomers isobenzofuran (IIIa) and isoindole (IVa). Whereas I and II were first prepared[1] many years ago and are very stable, IIIa is still unknown[2] and IVa has only recently been obtained[3] after a century of unsuccessful attempts.[4] Indded, IVa has still not been isolated, its existence as a transient reaction intermediate being inferred only from the production of Diels–Alder adducts when IV is formed in the presence of dienophiles. Likewise the few derivatives of III and IV that have been isolated (1-arylisoindoles[5] (IVb), 1,3-diphenylisobenzofuran[2c] (IIIb), and 1,3-diphenylisoindole[2c] (IVc)) are very reactive and polymerize or undergo Diels–Alder reactions with exceptional ease.

Earlier theoretical studies[6], using the HMO method, failed to account for these differences. The calculated[7] delocalization energies and charge densities of IVa and isoindolenine (V) also failed to provide any satisfactory explanation for the instability of IVa. The HMO method is of course known[8] to be very unreliable for molecules



I



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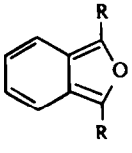
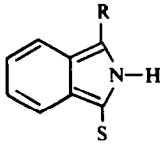
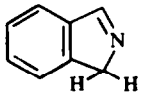


III: a, R=H
b, R=Ph



IV: a, R=S=H
b, R=aryl
S=H
c, R=S=Ph



V

* Part XX: M. J. S. Dewar and N. Trinajstić, *J. Am. Chem. Soc.* **92**, 1453 (1970).

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containing heteroatoms; we therefore decided to reinvestigate this problem using a more refined treatment. An obvious choice for this was the semiempirical SCF MO π approximation recently developed in these laboratories[9], for this has been shown to give excellent estimates of the heats of atomization of conjugated molecules of all kinds derived from carbon, nitrogen, and oxygen. Here we describe calculations for I–IV, and some related compounds using this approach.

THEORETICAL METHOD

The theoretical procedure has been described in detail in earlier papers[9]. It is a semiempirical SCF MO Π approximation, based on the Pople method,[10] in which the contributions of σ bonds are written as sums of bond energies and compression energies, the latter estimated from Morse functions. Bond lengths are recalculated at each step in the iterative SCF procedure, using assumed linear relations between bond order and bond length, and the corresponding two-center integrals recalculated accordingly (variable β procedure[9b]). In the case of bonds involving dissimilar atoms, allowance is made for the effect of polarity in the intervening σ bonds[9e]; the parameters used were those of Part XII[9e]. Ionization potentials were estimated either from Koopmans theorem, or by difference, the energies of the ions being calculated by the "half-electron" method.[11]

Earlier studies had shown[9c,d] that the calculated heats of atomization of classical conjugated polyenes can be expressed accurately as sums of bond energies, implying that the bonds in such compounds are localized[8]; the corresponding "polyene" C—C and C=C bond energies naturally differ from those anticipated for "pure single" or "pure double" bonds, but they are the same in polyenes of different types. This result leads to a simple definition[8, 9c,d] of resonance energy as the difference in heat of atomization between a given hydrocarbon and a corresponding classical polyene (e.g. benzene and 1,3,5-hexatriene), that of the latter being estimated as a sum of "polyene" bond energies. Subsequent work[12] showed that this definition could be extended to compounds containing nitrogen and/or oxygen, the heats of atomization of classical heteroconjugated molecules also being representable as additive sums of bond energies.

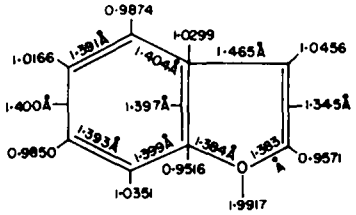
RESULTS AND DISCUSSION

Table 1 shows in diagrammatic form the results of calculations for benzofuran (I), indole (II), isobenzofuran (IIIa), 1-phenylisoindole (IVb), 1,3-diphenylisoindole (IVc), isoindole (IVa), 1,3-diphenylisobenzofuran (IIIb), furan (VI), pyrrole (VII), dibenzofuran (VIII), carbazole (IX), benzo[*f*]isoindole (XI), benzo[*e*]indole (XII), benzo[*e*]isoindole (XIII), benzo[*g*]indole (XIV), dibenzo[*e,g*]indole (XV), and dibenzo[*e,g*]isoindole (XVI). Bond lengths and π electron densities are listed on the formulae and heats of atomization at 25° ($\Delta H_a^{25°}$), resonance energies (E_R), and vertical (Koopmans theorem) $(IP)_v$ and adiabatic (half-electron method) $(IP)_a$ ionization potentials underneath the formulae. Experimental values, where available, are given in parentheses.

In cases where experimental data are available, the agreement with our calculated values for heats of atomization, bond lengths, and ionization potentials is good. Indeed, the discrepancies in the calculated heats of atomization are within the limits of experimental error and the discrepancies in bond lengths are also small (<0·02Å).

The calculated resonance energies also seem to be in good agreement with the observed chemistry of these compounds. Thus furan (VI) is predicted to be virtually nonaromatic, having a negligible resonance energy (1·6 kcal/mole) and CC bond lengths close to the values calculated for classical polyenes (1·345Å, 1·464Å). Furan behaves like a typical 1,3-diene, undergoing Diels–Alder reactions with great ease.[13] Pyrrole (VII), on the other hand, is predicted to be aromatic, having a significant resonance energy (8·4 kcal/mole) and CC bond lengths that differ significantly from the values characteristic of polyenes; the chemistry of pyrrole, in particular its failure to undergo addition reactions[14] indicates it to be aromatic. Likewise the resonance energy calculated for benzofuran (I) is almost identical with that of benzene, implying that the 5-membered ring in I is not aromatic, whereas the resonance energy calculated for indole (II) is significantly greater; benzofuran resembles styrene in its chemistry whereas indole is less prompt to undergo addition reactions. Indole is, however, less aromatic in this sense than pyrrole, as would be expected from our calculations, since

TABLE 1. CALCULATED BOND LENGTHS, CHARGE DENSITIES, HEATS OF ATOMIZATION AT 25° ($-\Delta H_a^{25°}$), RESONANCE ENERGIES (E_R), ADIABATIC AND VERTICAL IONIZATION POTENTIALS ($(IP)_a$, $(IP)_v$). FOR DESCRIPTION OF CALCULATIONS SEE TEXT: (EXPERIMENTAL DATA, WHERE AVAILABLE, PRESENTED IN PARENTHESES)



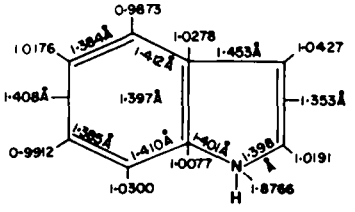
I

$-\Delta H_a^{25°}$ = 75·38 eV

E_R = 20·3 kcal/mole

$(IP)_a$ = 8·60 eV/8·29 eV/[a,b]

$(IP)_v$ = 8·99 eV/8·36 eV/[a]



II

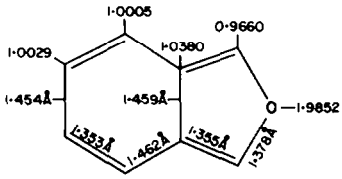
$-\Delta H_a^{25°}$ = 78·43 eV/78·06 eV/[c]

E_R = 23·8 kcal/mole

$(IP)_a$ = 8·36 eV/7·75 eV/[a,d]

$(IP)_v$ = 8·70 eV/7·90 eV/[a]

TABLE 1 (*cont.*)



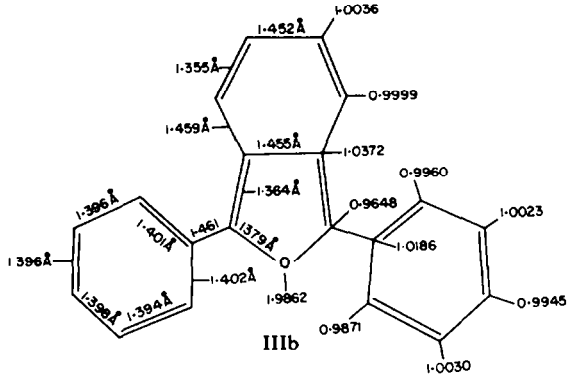
IIIa

$-\Delta H_a^{25°} = 74{\cdot}60$ eV

$E_R = 2{\cdot}4$ kcal/mole

$(IP)_a = 7{\cdot}91$ eV

$(IP)_v = 8{\cdot}17$ eV



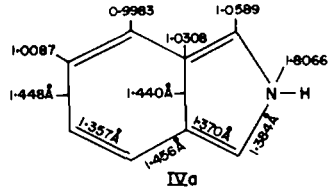
IIIb

$-\Delta H_a^{25°} = 179{\cdot}92$ eV

$E_R = 43{\cdot}8$ kcal/mole

$(IP)_a = 7{\cdot}09$ eV

$(IP)_v = 7{\cdot}63$ eV



IVa

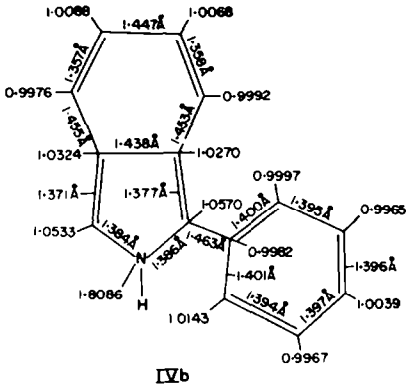
$-\Delta H_a^{25°} = 77{\cdot}90$ eV

$E_R = 11{\cdot}6$ kcal/mole

$(IP)_a = 7{\cdot}81$ eV

$(IP)_v = 8{\cdot}07$ eV

TABLE1 (*cont.*)



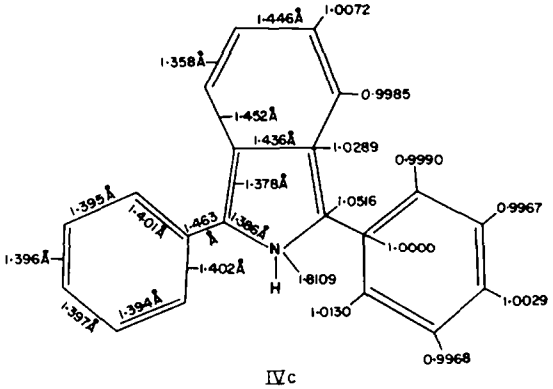
IVb

$-\Delta H_0^{25°} = 130{\cdot}54$ eV

$E_R = 31{\cdot}7$ kcal/mole

$(IP)_a = 7{\cdot}44$ eV

$(IP)_v = 7{\cdot}81$ eV



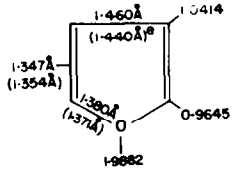
IVc

$-\Delta H_0^{25°} = 183{\cdot}17$ eV

$E_R = 51{\cdot}9$ kcal/mole

$(IP)_a = 7{\cdot}13$ eV

$(IP)_v = 7{\cdot}60$ eV



VI

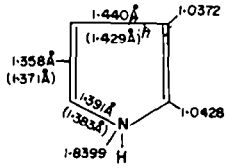
$-\Delta H_0^{25°} = 41{\cdot}56$ eV/41·52 eV/[f]

$E_R = 1{\cdot}6$ kcal/mole

$(IP)_a = 9{\cdot}02$ eV/8·90 eV/[e]

$(IP)_v = 9{\cdot}23$ eV/9·03 eV/[g]

TABLE 1 (*cont.*)



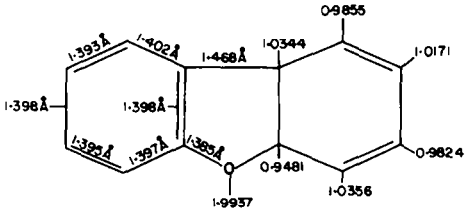
VII

$-\Delta H_a^{25°}$ = 44·76 eV/44·77 eV/[c]

E_R = 8·4 kcal/mole

$(IP)_a$ = 8·90 eV/8·20 eV/[a,i]

$(IP)_v$ = 9·10 eV/8·97 eV/[j]



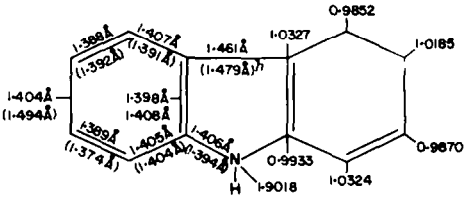
VIII

$-\Delta H_a^{25°}$ = 109·22 eV/109·18 eV/[k]

E_R = 39·9 kcal/mole

$(IP)_a$ = 8·37 eV/8·20 eV/[a,l]

$(IP)_v$ = 8·71 eV/8·20 eV/[a,m]



IX

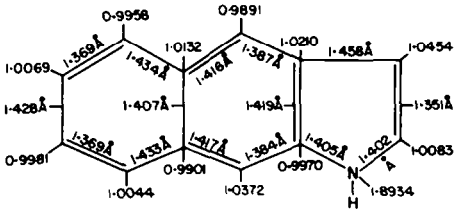
$-\Delta H_a^{25°}$ = 112·17 eV/111·91 eV/[c]

E_R = 40·9 kcal/mole

$(IP)_a$ = 8·25 eV

$(IP)_v$ = 8·58 eV

TABLE 1 (*cont.*)



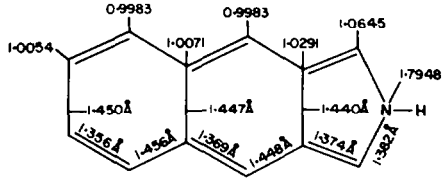
X

$-\Delta H_a^{25°} = 111{\cdot}80$ eV

$E = 32{\cdot}3$ kcal/mole

$(IP)_a = 7{\cdot}84$ eV

$(IP)_v = 8{\cdot}16$ eV



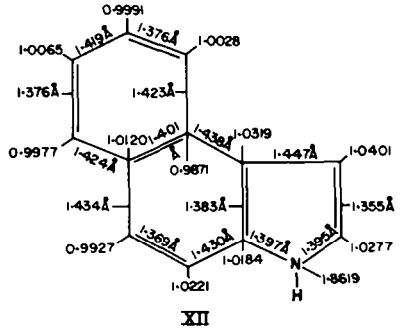
XI

$-\Delta H_a^{25°} = 111{\cdot}03$ eV

$E_R = 14{\cdot}6$ kcal/mole

$(IP)_a = 7{\cdot}21$ eV

$(IP)_v = 7{\cdot}53$ eV



XII

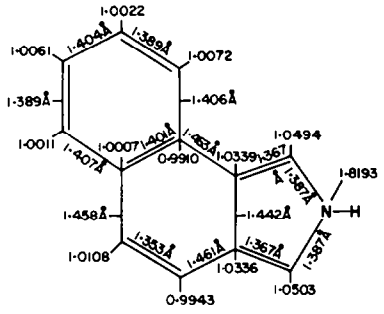
$-\Delta H_a^{25°} = 111{\cdot}96$ eV

$E_R = 36{\cdot}0$ kcal/mole

$(IP)_a = 7{\cdot}96$ eV

$(IP)_v = 8{\cdot}30$ eV

TABLE 1 (*cont.*)



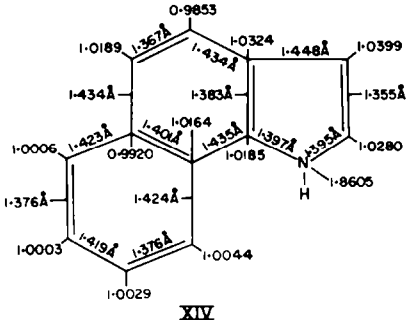
XIII

$-\Delta H_a^{25°} = 111{\cdot}64$ eV

$E_R = 30{\cdot}0$ kcal/mole

$(IP)_a = 7{\cdot}78$ eV

$(IP)_v = 8{\cdot}13$ eV



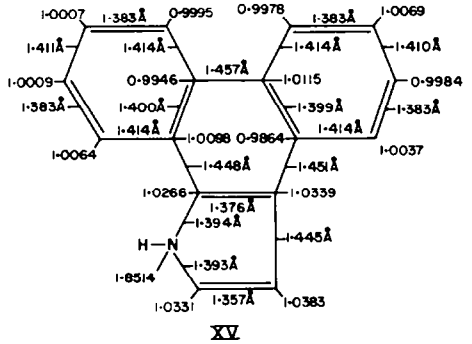
XIV

$-\Delta H^{25°} = 111{\cdot}96$ eV

$E_R = 36{\cdot}0$ kcal/mole

$(IP)_a = 8{\cdot}11$ eV

$(IP)_v = 8{\cdot}41$ eV



XV

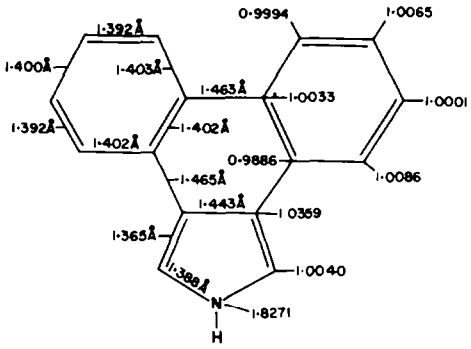
$-\Delta H_a^{25°} = 145{\cdot}62$ eV

$E_R = 51{\cdot}2$ kcal/mole

$(IP)_a = 7{\cdot}89$ eV

$(IP)_v = 8{\cdot}25$ eV

TABLE 1 (*cont.*)



XVI

$-\Delta H_g^{25°}$ = 145·43 eV

E_R = 46·8 kcal/mole

$(IP)_a$ = 7·82 eV

$(IP)_v$ = 8·17 eV

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[a] J. H. D. Eland, *J. Mass Spectrometry and Ion Physics* **2**, 471 (1969)

[b] Experimental result obtained by us is 8·42 eV; the photoelectron spectrometer employed has been described elsewhere (M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.* **50**, 654 (1969)

[c] H. Zimmermann and H. Geisenfelder, *Z. Electrochem.* **65**, 368 (1961)

[d] Our experimental value is 7·78 eV

[e] B. Bak, L. Hansen and J. Rastrup-Andersen, *Disc. Faraday Soc.* **19**, 30 (1955)

[f] G. W. Wheland, *Resonance in Organic Chemistry*, Wiley, New York (1955)

[g] I. Omura, K. Higasi and H. Baba, *Bull. Chem. Soc. Japan* **29**, 501, 521 (1956)

[h] B. Bak, D. Christensen, L. Hansen and J. Rastrup-Andersen, *J. Chem. Phys.* **24**, 720 (1956)

[i] Our experimental result is 8·22 eV

[j] I. Omura, H. Baba and K. Higasi, *J. Phys. Soc. Japan* **10**, 317 (1955)

[k] R. C. Cass, S. E. Fletcher, C. T. Mortimer, H. P. Springall and T. R. White, *J. Chem. Soc.* 1406 (1958)

[l] Our experimental result is 8·22 eV

[m] This value should be larger because vertical and adiabatic ionization potentials usually differ for 0·3 eV

[n] M. Kurahashi, M. Fukuyo, A. Shimada, A. Furusaki and I. Nitta, *Bull. Chem. Soc. Japan* **42**, 2174 (1969)

the difference in resonance energy between indole and benzene (3·8 kcal/mole) is less than half that of pyrrole (8·4 kcal/mole). The calculated difference in resonance energy between dibenzofuran (VIII) and carbazole (IX) is even smaller (1·0 kcal/mole), both values being close to that for biphenyl (39·0 kcal/mole); the chemistry of VIII and IX differs little from that of diphenylether (40·5 kcal/mole) and diphenylamine (39·2 kcal/mole) respectively.

Our calculated resonance energies imply that isobenzofuran (IIIa) should be very much less stable than the isomeric benzofuran (I); indeed, IIIa is predicted to be almost nonaromatic, having a very small resonance energy (2·4 kcal/mole) and CC bond lengths close to the "polyene" values. This of course would explain why attempts

to prepare IIIa have so far proved unsuccessful; for addition of any reagent to the 1 or 3 positions of IIIa should lead to a great increase (18 kcal/mole) in resonance energy, the six-membered ring being quinonoid in IIIa but benzenoid in the adduct. Calculations are also reported for 1,3-diphenylisobenzofuran (IIIb). The difference in resonance energy between this and IIIa (41·4 kcal/mole) is barely more than twice the resonance energy of benzene (20·0 kcal/mole[9d]) and the predicted bond lengths in the isobenzofuran moieties of IIIa and IIIb are very similar; while IIIb, unlike IIIa, has been isolated,[2c] it is extremely reactive.

Isoindole (IVa) is likewise predicted to be much less stable than indole (II); here, however, the difference in resonance energy (12·2 kcal/mole) is much less than that between IIIa and I (17·9 kcal/mole) and addition to the 1 or 3 positions of IVa should head to a much smaller increase in resonance energy (8·6 kcal/mole). Indeed, isoindole (IVa) is predicted to be still an aromatic system, having quite a large resonance energy (11·6 kcal/mole) and bond lengths which differ appreciably from the "polyene" values. As pointed out above, the experimental evidence certainly suggests that IVa is much more stable than IIIa; for while IVa has not been isolated, its existence as a reaction intermediate has at least been established.[3, 5, 15] Similar conclusions follow for the 1-phenyl (IVb) and 1,3-diphenyl (IVc) derivatives of IVa, both of which are extremely reactive;[2c, 5] our calculated differences in resonance energy between IVb and IVa (20·3 kcal/mole) and between IVc and IVa (40·3 kcal/mole) are almost exactly those calculated for one (20·0 kcal/mole) and two (40·1 kcal/mole) molecules of benzene, implying that phenyl substituents in the 1- and 3- positions of IVa should have virtually no stabilizing effect.

Table 1 also lists values for the seven isomeric tricyclic compounds VIII–XIV. Of these VIII and IX are predicted to be the most stable, as would be expected since they alone contain two discrete benzene rings. The resonance energy of two molecules of benzene is much greater than that of naphthalene, the difference being greater than that between indole and benzene. The three benzoindoles X, XII, and XIV are predicted to be of comparable stability, as might be expected on the basis of naïve resonance theory since three uncharged classical structures can be written for each of them. On the other hand benzo[*e*]isoindole (XIII), for which two classical structures can be written, is predicted to be much more stable than benzo[*f*]isoindole (XI), for which there is but one classical structure; the bond lengths calculated for XI imply strong bond fixation over the entire molecule and the calculated resonance energy is much less than that for benzene. These results lead to the prediction that XIII should be a relatively stable compound, its resonance energy being only 6 kcal/mole less than that of the isomeric indole (XII); XIII can indeed be regarded as 3-phenylindole in which a localized ethylene bridge connects the two rings. The bond lengths calculated for XIII correspond closely to those expected for such a structure and the resonance energy of XIII is close to the sum (28·4 kcal/mole) of those for benzene and pyrrole. On the other hand XI should be much less stable, although the calculated resonance energy and bond lengths imply that it should still be weakly aromatic.[16]

Our calculations lead to the prediction that the resonance energies of XII and XIV (36·0 kcal/mole), where pyrrole is annelated to naphthalene via the 1,2 bond in the latter, should be significantly greater than that of X (32·3 kcal/mole), where annelation involves the 2,3 bond. Indeed, whereas the former value is greater than that of naphthalene, implying that the pyrrole ring in XII and XIV is aromatic (cf. indole/ben-

zene), the latter value is *less*. Here again a naïve explanation can be given in terms of the extensive fixation of bonds in pyrrole (VII). The 2,3 bond in VII is close to double in length; annelation of pyrrole via this bond should be facilitated if the bond to which annelation takes place is also short. Since the 1,2 bond in naphthalene is shorter than the 2,3, annelation to give XII or XIV is more favorable than annelation to give X. It must be admitted that this argument would lead to the incorrect prediction that XI should be more stable than XIII; one would have to add a proviso that this is a small second order effect, subservient to the distinction between aromatic and nonaromatic systems. It does, however, lead to the prediction, supported by our calculations, that XVI should be an exceptionally stable "isoindole"; for the 9,10 bond in phenanthrene has an exceptionally high bond order. The difference between our calculated resonance energies for XVI and the isomeric indole XV is only 4·4 kcal/mole.

These predictions are supported by the recent isolation of XVI.[17]

One final amusing prediction is concerned with ionization potentials; our calculations imply that the ionization potential of isobenzofuran (IIIa) should be less than that of benzofuran (I), and that the ionization potentials of the isoindoles IVa, XI, XIII, and XVI should be likewise less than those of the corresponding indoles II, X, XII (or XIV) and XV. The differences are moreover predicted to run parallel to the differences in stability between the pairs of isomers in question. No experimental data are as yet available to test this prediction.

In conclusion, it should be pointed out that the procedure used here has proved reliable in every connection in which it has so far been applied; it would therefore seem advisable to examine its predictions before undertaking the synthesis of any novel potentially aromatic systems. The calculations are straightforward and require little computer time; our computer program is available through the Quantum Chemistry Program Exchange at Indiana University.

REFERENCES

1 [a] A. G. Perkin, *J. Chem. Soc.* **23**, 368 (1870); *Ibid.* **24**, 295 (1871);
[b] A. Baeyer, *Liebigs Ann.* **140**, 295 (1866)

2 [a] R. M. Acheson, *An Introduction to the Chemistry of Heterocyclic Compounds* p. 153. Interscience, New York (1960);
[b] R. C. Elderfield, *Heterocyclic Compounds* (Edited by R. C. Elderfield) Vol. II, Chap. 2, p. 68. Wiley, New York (1951);
[c] M. E. Mann and J. D. White, *Chem. Comm.* 420 (1969)

3 R. Kreher and J. Seubert, *Z. Naturforschg.* **20b**, 75 (1965)

4 [a] S. Gabriel and A. Neumann, *Ber. Dtsch. Chem. Ges.* **26**, 705 (1893);
[b] R. E. Rose, *J. Am. Chem. Soc.* **33**, 390 (1911);
[c] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.* 3295 (1928)

5 D. F. Veber and W. Lwowski, *J. Am. Chem. Soc.* **85**, 646 (1963); *Ibid.* **86**, 4152 (1964)

6 [a] M. J. S. Dewar, *Trans. Faraday Soc.* **42**, 764 (1946);
[b] H. C. Longuet-Higgins and C. A. Coulson, *Ibid.* **43**, 87 (1947)

7 J. Kopecky, J. E. Shields, and J. Bornstein, *Tetrahedron Letters* 3669 (1967)

8 M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry* McGraw-Hill, New York (1969)

9 [a] A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.* **42**, 756 (1965);
[b] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.* **87**, 685 (1965);
[c] M. J. S. Dewar and G. J. Gleicher, *Ibid.* **87**, 692 (1965);
[d] M. J. S. Dewar and C. de Llano, *Ibid.* **91**, 789 (1969);
[e] M. J. S. Dewar and T. Morita, *Ibid.* **91**, 796 (1969)

[10] J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953)
[11] M. J. S. Dewar, J. A. Hashmall and C. G. Venier, *J. Am. Chem. Soc.* **90**, 1953 (1968)
[12] [a] M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc.* A 1754 (1968);
[b] M. J. S. Dewar, A. J. Harget and N. Trinajstić, *J. Am. Chem. Soc.* **91**, 6321 (1969)
[13] R. B. Woodward and H. Baer, *Ibid.* **70**, 1161 (1948)
[14] [a] L. Mandell and W. A. Blanchard, *Ibid.* **79**, 6198 (1957);
[b] R. M. Acheson and J. M. Vernon, *J. Chem. Soc.* 1148 (1962)
[15] J. C. Emmett and W. Lwowski, *Tetrahedron* **22**, 1011 (1966)
[16] J. E. Shields and J. Bornstein, *Chem. Ind.* 1404 (1967)
[17] J. E. Shields and J. Bornstein, *J. Am. Chem. Soc.* **91**, 5192 (1969)