The Electronic Structure of the Quinonoid Bicyclic Heterocycles Isoindole, Benzo[*c*]furan, Benzo[*c*]thiophen, and 2*H*-Indene

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Non-empirical calculations for the electronic ground and lowest triplet excited states for isoindole, benzo[*c*]furan, benzo[*c*]thiophen, and *N*-methylisoindole show that some resonance energy (RE) is present in these systems, and that their instability can be attributed to a combination of a low RE and a low-lying excited state. The photoelectron spectra are reported for the last three compounds, and the ionisation potentials are assigned in the light of the calculations. Detailed analysis of the ^{1}H n.m.r. spectra of these compounds supports the conclusions of low aromatic character.

PREVIOUSLY we reported non-empirical MO calculations of the ground states of various five- and six-membered ring, potentially aromatic, systems containing one or more of the heteroatoms, nitrogen, oxygen, phosphorus, or sulphur.[1-10] The benzo-derivatives of the five-membered ring heterocycles are of particular interest owing to the existence of the Kekulé like (1) and quinonoid (2) series.

Recently we reported [11] calculations of the electronic structure of the ground states of the Kekulé series (1) and

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[1] M. H. Palmer and A. J. Gaskell, *Theor. Chim. Acta*, 1971, **23**, 52.

[2] M. H. Palmer, A. J. Gaskell, and M. S. Barber, *Theor. Chim. Acta*, 1972, **26**, 357.

[3] S. Cradock, R. H. Findlay, and M. H. Palmer, *Tetrahedron*, 1973, **29**, 2173.

[4] M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *Tetrahedron Letters*, 1973, 4659.

[5] M. H. Palmer and R. H. Findlay, *Tetrahedron Letters*, 1974, 253.

[6] M. H. Palmer, A. J. Gaskell, and M. S. Barber, *J. Mol. Structure*, 1972, **12**, 197.

[7] M. H. Palmer and R. H. Findlay, *Tetrahedron Letters*, 1972, 4165.

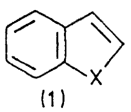
[8] M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *J.C.S. Perkin II*, 1974, 420.

[9] M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 778.

[10] M. H. Palmer and R. H. Findlay, *J.C.S. Perkin II*, 1974, 1885.

[11] M. H. Palmer and S. M. F. Kennedy, *J.C.S. Perkin II*, 1974, 1893.

now extend these results to the corresponding quinonoid compounds (2a—d) and compare them with both naphthalene (3) and the monocyclic systems (4a—c). Since



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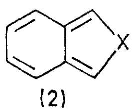

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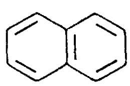
a ; X=NH
b ; X=O
c ; X=S
d ; X=NMe
e ; X=CH$_2$



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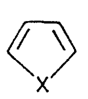

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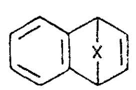

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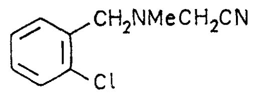

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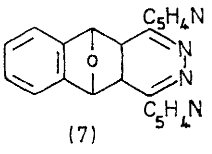

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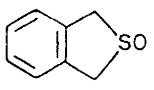

(8)

the relative instability of the quinonoid series could be attributed to either (a) a raised ground state energy (low resonance energy) or (b) a low lying excited state, we include calculations of the ground and first triplet excited state. We assign the photoelectron spectra of (2b—d) in the light of the ground state calculations. Finally we report a detailed analysis of the ^{1}H n.m.r. spectra of (2b—d) since relative values of the coupling constants have been used in discussions of aromatic character in related compounds (see below).

METHODS

Preparations.—We found the most satisfactory method for synthesis of isoindole (2a) was *via* (4; $X = NCO_2C_4H_9$) and (5; $X = NCO_2C_4H_9$),[12] but were unable to volatilise the material into the photoelectron spectrometer without extensive decomposition. *N*-Methylisoindole (2d) was prepared by a similar route, but conversion to (5; X = NMe) proceeded in very poor yield. The most successful route was from 2-chlorobenzyl chloride and methylaminoacetonitrile,[13] the intermediate (6) requiring purification from a range of by-products by spinning band column fractionation. Attempts at a reduction of *N*-methylphthalimide [14] always yielded a mixture of (2d) and the corresponding isoindoline. This same problem arose with attempts to dehydrate 2-ethylisoindoline *N*-oxide to 2-ethylisoindole.[15]

Benzo[*c*]furan was prepared from 1,4-epoxy-1,4-dihydronaphthalene (5; X = O) by two routes: (a) by interaction with 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine [16] and pyrolysis [17] of the adduct (7), but which yielded (2b) contaminated with 3,6-dipyridylpyridazine and (b) by reduction of the epoxide (5) to the corresponding 1,2,3,4-tetrahydronaphthalene (Pd–C; MeOH; 1 atm.) followed by thermolysis [18] through a silica tube (650°; 0.05 mmHg) with a liquid nitrogen trap.

Benzo[*c*]thiophen (2c) was obtained by thermolysis of the sulphoxide (8) mixed with alumina (150°; 5 mmHg).[19]

Photoelectron Spectra.—A Perkin-Elmer PS16 spectrometer, calibrated with the argon doublet at 15.75 and 15.93 eV (insert in Figure 1), was used.[11] In general only the first band in each compound showed appreciable fine structure, and this aspect was not pursued. The band assignments (Figure 1) are based upon the calculated orbital energies using Koopmans' theorem.[11] As in our work on the Kekulé

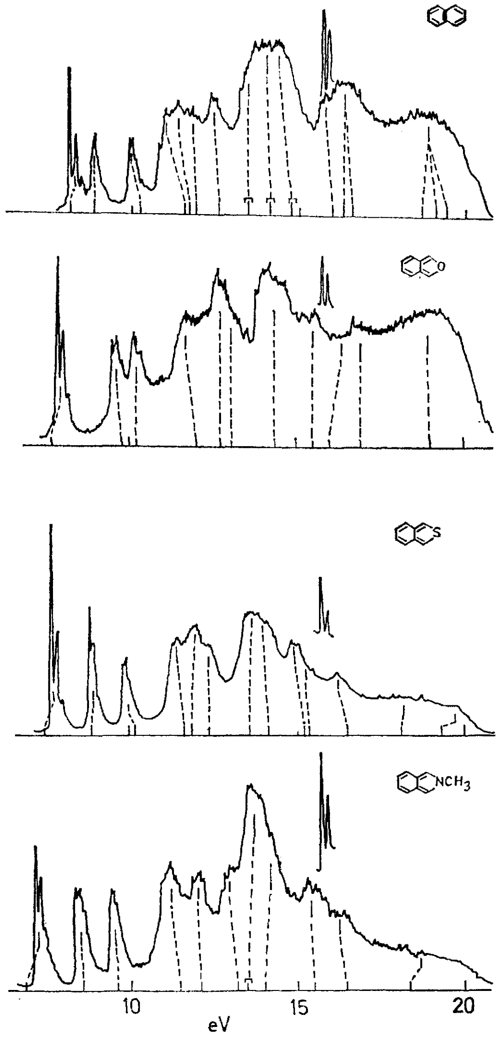

FIGURE 1 Photoelectron spectra (He^{I}) of naphthalene and the quinonoid heterocycles (2b—d)

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[12] L. A. Carpino and D. E. Barr, *J. Org. Chem.*, 1966, **31**, 764.

[13] B. Jaques and R. G. Wallace, *J.C.S. Chem. Comm.*, 1972, 397.

[14] D. L. Garmaise and A. Ryan, *J. Heterocyclic Chem.*, 1970, **7**, 413; G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Annalen*, 1951, **572**, 1; G. Wittig, G. Closs, and F. Mindermann, *ibid.*, 1955, **594**, 89.

[15] R. Kreher and J. Scubert, *Angew. Chem. Internat. Edn.*, 1964, **3**, 639; 1966, **5**, 967; J. K. Kochi and E. A. Singleton, *Tetrahedron*, 1968, **24**, 4649.

[16] J. F. Geldard and F. Lions, *J. Org. Chem.*, 1965, **30**, 318.

[17] R. N. Warrener, *J. Amer. Chem. Soc.*, 1971, **93**, 2346.

[18] U. E. Wiersum and W. J. Mijs, *J.C.S. Chem. Comm.*, 1972, 347.

[19] M. P. Cava, N. M. Pollock, O. A. Mamer, and M. J. Mitchell, *J. Org. Chem.*, 1971, **36**, 3932.

series[11] we endeavoured to obtain *X*-ray photoelectron spectra of the valency shell orbitals, but the quality of the spectra from the solid samples is low, and only in the case of benzo[*c*]thiophen were well resolved peaks obtained at 1 221 and 1 229 eV kinetic energy corresponding to $3s_S$ and $2s_C$ groupings respectively (relative to Mg-K_α 1 253 eV).

N.m.r. Spectra and Analysis.—^{1}H and ^{13}C n.m.r. spectra were measured using Varian HA 100 and XL-100 spectrometers. In the former case the spectra of (2b—d) were run at various temperatures in $CDCl_3$ solution (at 273, 273, and 253 K respectively). The samples were run under nitrogen or aqueous sodium dithionite [in the case of (2c)] to avoid air oxidation. In the ^{13}C spectra the assignments were confirmed by off-resonance decoupling, and are quoted in p.p.m. downfield from tetramethylsilane.

TABLE 1

Molecular energies for the systems

	Naphthalene	2*H*-Indene	Isoindole	Benzo[*c*]furan	Benzo[*c*]thiophen (*sp* Basis)	Benzo[*c*]thiophen (*spd* + $3s^1$)
Total energy (a.u.) [a]	−382.371 27	−344.522 94	−360.505 12	−380.1234	−702.312 40	−702.430 85
Binding energy (a.u.)	−2.290 27	−2.052 54	−1.866 72	−1.684 24	−1.697 80	
Resonance energy (calc.) (kJ mol^{-1})	357	72	252	147	217	259

[a] Energy conversion units (see ' Symbols, Signs, and Abbreviations,' The Royal Society, London, 1969) are 1 a.u. = 2 625.46 kJ mol^{-1}, 1 a.u. = 27.211 eV, 1 eV = 1.6021 × 10^{-19} J.

TABLE 2

Low lying triplet state excitation energies (eV)

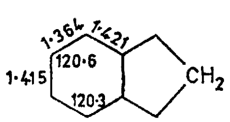
	Naphthalene	Indole	Benzo[*b*]furan	Benzo[*b*]thiophen
UHF	3.028	3.206	2.640	3.431
RHF	4.420	4.146	3.647	4.350
Expt.	2.665 [a]	30.6,[b] 3.069 [c]		2.972,[d] 2.965 [e]
INDO		6.549	5.897	4.134
	2*H*-Indene	Isoindole	Benzo[*c*]furan	Benzo[*c*]thiophen
UHF	0.884	2.400	0.286	1.972
RHF	1.162	2.694	0.593	2.425
INDO		4.062	3.521	3.727

[a] H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 470. [b] G. S. Kembrowskii, V. P. Bobrovich, and S. V. Koneve, *Zhur. Priklad. Spektroskopii*, 1966, **5**, 695. [c] R. C. Heckman, *J. Mol. Spectroscopy*, 1958, **2**, 27; P.-S. Song and W. E. Kurtin, *J. Amer. Chem. Soc.*, 1969, **91**, 4892. [d] D. F. Evans, *J. Chem. Soc.*, 1959, 2753. [e] M. R. Padhye and J. C. Patel, *J. Sci. Ind. Res., India*, 1956, **15B**, 171, 206.

Computer analysis of the ^{1}H n.m.r. $AA^1BB^1XX^1$ spectra was carried out by means of the program LAMS (C. W. Haigh, Swansea). The analysis took place in two stages. (1) An AA^1BB^1 analysis was completed to yield the lowest root mean square deviation in transition frequencies; a series of non-iterative studies of the $AA^1BB^1XX^1$ system were made with selected values of the additional coupling constants. (2) A full six-spin analysis was performed on the most promising set of parameters. In the case of (2b), the 1-H–3-H coupling was removed by double irradiation in stage (1), but this could not be done for (2c and d) owing to the proximity of these to the 4—7-H multiplets.

Computations.—We used the same basis of *scaled* ' best atom ' gaussian functions (GTOs) as in our recent work.[2,5,7,10,11] These consisted of five, two, three, and three GTOs for $1s_X$, $2s_X$, $2p_X$ (where X = C, N, or O), and $1s_H$ respectively, while sulphur was represented by six, two, two, four, two, and one GTOs for 1*s*, 2*s*, 3*s*, 2*p*, 3*p*, and 3*d* respectively. The free atom energies (a.u.) using the unscaled ' best atom ' basis, the Hartree–Fock limit,[20] and the percentage of the latter are: H(^{2}S), −0.4970, −0.5000 (99.4); C(^{3}P), −37.6106, −37.6886 (99.8); N(^{4}S), −56.2754, −57.4009 (99.8); O(^{3}P), −74.6121, −74.8094 (99.7); S(^{3}P), −396.7476, −397.5048 (99.8). The computations were executed with the ATMOL-2 system of programs on an IBM 370/195 computer,* and the main results are shown in Tables 1—5.*

Geometric Parameters.—There is no experimental information for (2a—e).† We thus constructed geometries based upon the fusion of one half of naphthalene with the corresponding heterocycle, the actual values being shown in (9)—(12). This procedure had the additional computational advantage that many electron repulsion integrals (relating to the naphthalene portion) could be used in several calculations. The orientation of the *N*-methyl group in (2d) was



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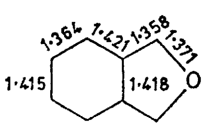

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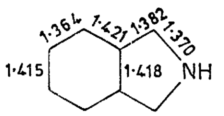

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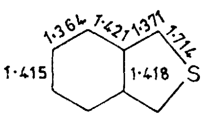

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* Additional data are contained in Supplementary Publication No. SUP 21518 (10 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

† Various workers[21,22] have calculated bond lengths for (2a—c) based upon self-consistent bond order–bond length relationships; these calculations do *not* lead to values for the bond angles and are thus insufficient for the present work.

[20] E. Clementi ' Tables of Atomic Functions,' in *IBM J. Res. Development*, 1965, **9**, 2.

[21] (*a*) M. J. S. Dewar, A. J. Harget, N. Trinajstic, and S. D. Worley, *Tetrahedron*, 1970, **26**, 4505; (*b*) M. J. S. Dewar and N. Trinajstic, *J. Amer. Chem. Soc.*, 1970, **92**, 1453.

[22] J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, 1968, **72**, 3975.

chosen to have a σ–π separation (a′/a″ respectively in C_s symmetry).

TABLE 3

Molecular orbital energy levels (eV) for 2*H*-indene, isoindole, benzo[*c*]furan, benzo[*c*]thiophen, and *N*-methylisoindole

Energy	Character
	Isoindole
a_1	
425.7	$1s_{\mathrm{N}}$
307.1	$1s_{1+3}$
306.4	$1s_{4+7}$
306.4	$1s_{3a+7a}$
306.2	$1s_{5+6}$
35.49	$2s_{\mathrm{N}} + 2s_{\mathrm{C}}(a_{1g})$
30.98	$2s_{\mathrm{C}} - 2s_{\mathrm{N}}(b_{3u})$
28.12	$2s_{\mathrm{C}}(a_{1g})$
23.68	$2s_{\mathrm{C}} + 2p_{\mathrm{C}}(\mathrm{L}, b_{3u})$
21.19	$\mathrm{CC}_{3a,7a} + \mathrm{CH}(\mathrm{T}, a_{1g})$
20.00	$\mathrm{CH}_{1,3} + \mathrm{NH}(b_{3u})$
18.44	$\mathrm{CC} + \mathrm{CH}(\mathrm{L}, a_{1g})$
16.41	$\mathrm{CH} + \mathrm{CN}(\mathrm{L} + \mathrm{T}, b_{3u})$
15.34	$\mathrm{CC}(\mathrm{L} + \mathrm{T}, b_{3u})$
b_2	
307.1	$1s_{1-3}$
306.4	$1s_{4-7}$
306.4	$1s_{3a-7a}$
306.2	$1s_{5-6}$
27.82	$2s_{\mathrm{C}}(b_{2u})$
26.04	$2s_{\mathrm{C}}(b_{1g})$
21.59	$\mathrm{CC} + \mathrm{CN}(b_{2u})$
17.87	$\mathrm{CC} + \mathrm{CH}(b_{1g})$
16.24	$\mathrm{CC} + \mathrm{CH}(\mathrm{T}, b_{1g})$
15.95	$\mathrm{CC} + \mathrm{CH}(\mathrm{T}, b_{1g})$
13.98	$\mathrm{CC}(\mathrm{L}, b_{1g})$
b_1	
16.68	$\mathrm{CC} + \mathrm{CN}(b_{1u})$
13.55	$\mathrm{CN}(b_{2g})$
9.53	$\mathrm{CC} + \mathrm{N}(b_{1u})$
a_2	
10.64	$\mathrm{CC}(b_{3g})$
7.23	$\mathrm{CC}(a_{1u})$

Energy	Character
	Benzo[*c*]furan
a_1	
562.7	$1a_2$
308.7	$1s_{1+3}$
307.4	$1s_{3a+7a}$
307.2	$1s_{4+7}$
307.0	$1s_{5+6}$
40.30	$2s_2$
32.15	$2s_{\mathrm{C}}$
29.34	$2s_{\mathrm{C}}$
24.08	$2s_{\mathrm{C}}$
22.00	$\mathrm{CH} + \mathrm{CC}(\mathrm{T}, a_{1g})$
20.11	$\mathrm{CH} + \mathrm{CC}(\mathrm{L} + \mathrm{T}, b_{3u})$
18.33	$\mathrm{CC}(\mathrm{L}, b_{1g})$
16.72	$\mathrm{CC} + \mathrm{CO}(\mathrm{L} + \mathrm{T}, a_{1g})$
15.12	$\mathrm{CC} + \mathrm{O}(\mathrm{L}, b_{3u})$
b_2	
308.8	$1s_{1-3}$
	Benoz[*c*]furan
307.4	$1s_{3a-7a}$
307.2	$1s_{4-7}$
307.0	$1s_{5-6}$
28.75	$2s_{\mathrm{C}}(b_{2c})$
26.87	$2s_{\mathrm{C}}(b_{1g})$
22.38	$\mathrm{CO}(b_{2u})$
18.93	$\mathrm{CO} + \mathrm{CC}(\mathrm{L} + \mathrm{T}, b_{1g})$
17.15	$\mathrm{CH} + \mathrm{CO}(\mathrm{T}, b_{1g})$
16.70	$\mathrm{CH} + \mathrm{CC}(\mathrm{L} + \mathrm{T}, b_{1g})$
14.71	$\mathrm{CH} + \mathrm{CC}(\mathrm{L}, b_{1g})$
b_1	
18.20	$\mathrm{CO} + \mathrm{CC}(b_{1u})$
14.58	$\mathrm{CC}(b_{2g})$
10.89	$\mathrm{CC}(b_{1u})$
a_2	
11.53	$\mathrm{CC}(b_{3g})$
8.06	$\mathrm{CC}(a_{1u})$

Energy	Character
	Benzo[*c*]thiophen (*spd* + $3s^1$ basis)
a_1	
2 495	$1s_2$
307.2	$1s_{3a+7a}$
307.1	$1s_{1-3}$
306.8	$1s_{4-7}$
306.7	$1s_{5-6}$
238.3	$2s_2$
180.9	$2p_2$
32.82	$2s_{\mathrm{C}} + 3s_2\ (\mathrm{a}_{1g})$
30.49	$2s_{\mathrm{C}}(b_{3u})$
26.99	$2s_{\mathrm{C}}(a_{1g})$
22.92	$2s_{\mathrm{C}} + 2p_{\mathrm{C}}(\mathrm{L}, b_{3u})$
21.45	$\mathrm{CC}_{3a,7a} + \mathrm{CH}(\mathrm{T}, b_{3u})$
19.33	$\mathrm{CH} + \mathrm{CC}(\mathrm{T}, b_{3u})$
17.70	$\mathrm{CH} + \mathrm{CC}(\mathrm{L})$
16.12	$\mathrm{CH} + \mathrm{CC}(\mathrm{T}, a_{1g})$
13.55	$\mathrm{CS} + \mathrm{CH} + \mathrm{CC}(\mathrm{L} + \mathrm{T})$
13.29	$\mathrm{CS} + \mathrm{CC}(\mathrm{L} + \mathrm{T}, a_{1g})$
	Benzo[*c*]thiophen (*spd* + $3s_1$ basis)
b_2	
307.2	$1s_{3a-7a}$
307.1	$1s_{1-3}$
306.8	$1s_{4-7}$
306.7	$1s_{5-6}$
180.9	$2p_2$
28.41	$2s_{\mathrm{C}}(b_{2u})$
26.04	$2s(b_{1g})$
21.43	$\mathrm{CC}(\mathrm{L}, b_{2u})$
17.89	$\mathrm{CC}(\mathrm{L}, b_{1g})$
16.51	$\mathrm{CH}_{4-7}(\mathrm{T})$
15.46	$\mathrm{CH}_{1-3}(\mathrm{Y})$
14.09	$\mathrm{CS} + \mathrm{CC}(\mathrm{L}, b_{1g})$
b_1	
180.8	$2p_2$
15.86	$\mathrm{CC} + \mathrm{CS}(b_{1u})$
13.16	$\mathrm{CC} + \mathrm{CS}(b_{2g})$
9.69	$\mathrm{CC}(b_{1u})$
a_2	
11.29	$\mathrm{CC}(b_{3g})$
7.84	$\mathrm{CC}(a_{1u})$

TABLE 3 (*Continued*)

Energy	Character
	N-Methylisoindole
a_1	
425.9	$1s_2$
308.2	$1s_{\mathrm{C(Me)}}$
306.9	$1s_1$
306.8	$1s_3$
306.3	$1s_4$
306.3	$1s_7$
306.3	$1s_{7a}$
306.2	$1s_{3a}$
306.1	$1s_6$
306.1	$1s_5$
35.68	$2s_2(a_1)$
31.05	$2s_{\mathrm{C}}(a_1)$
28.82	$2s_{\mathrm{C}}(a_1)$
27.75	$2s_{\mathrm{C}}(b_2)$
26.03	$2s_{\mathrm{C}}(b_2)$
25.93	$\mathrm{CH}_{\mathrm{Me}}(a_1)$
22.49	$\mathrm{CH} + \mathrm{CC}(a_1)(\mathrm{T})$
21.66	$\mathrm{CN} + \mathrm{CC}(b_2)(\mathrm{L} + \mathrm{T})$
20.83	$\mathrm{CH} + \mathrm{CC}(a_1)(\mathrm{T})$
	N-Methylisoindole
19.27	$\mathrm{CH} + \mathrm{CC}(a_1)(\mathrm{T})$
18.70	$\mathrm{CN} + \mathrm{CC}(b_2)(\mathrm{L} + \mathrm{T})$
17.88	$\mathrm{CC} + \mathrm{CH}$
16.46	$\mathrm{CH}(b_2)(\mathrm{T})$
16.10	$\mathrm{CC} + \mathrm{CN}(a_1)(\mathrm{L} + \mathrm{T})$
15.89	$\mathrm{CH} + \mathrm{CC}(b_2)(\mathrm{L} + \mathrm{T})$
15.60	$\mathrm{CN} + \mathrm{CH}_{\mathrm{Me}}(b_2)\ (\mathrm{T})$
15.12	$\mathrm{CH} + \mathrm{CC}(a_1)(\mathrm{L})$
13.73	$\mathrm{CH} + \mathrm{CC}(b_2)\ (\mathrm{L})$
12.71	$\mathrm{CH} + \mathrm{CC}(b_2)\ (\mathrm{T})$
a^{11}	
18.04	$\mathrm{N} + \mathrm{CH}_2(b_1)$
15.42	$\mathrm{CC} + \mathrm{CH}_2(b_1)$
13.16	$\mathrm{CN} + \mathrm{CC}(b_1)$
10.55	$\mathrm{CC}(a_2)$
9.26	$\mathrm{N} + \mathrm{CC}(b_1)$
7.14	$\mathrm{CC}(a_2)$

RESULTS AND DISCUSSION

Molecular and Resonance Energies.—Comparison of the quinonoid series total energies (Table 1) with the corresponding Kekulé isomers [11] shows that the former series are considerably destabilised. The resonance energies (kJ mol^{-1}) gave a simple direct measure of this, and data

TABLE 4

Total dipole moments (μ/D) π-electron average position ($\bar{r}$/Å) and second moments ($\bar{r}^2$)

	2*H*-Indene	Isoindole	*N*-Methylisoindole
μ(D)	0.952	2.940	3.428
π_1 [a–c]	0.130	0.200	−0.213
π_2	−0.267	−0.173	−0.387
π_3	−0.387	−0.183	−0.611
π_4	−0.221	−0.656	−0.614
π_5	2.101	1.469	1.403
π_6			2.526
Electronic component			
$\langle z^2 \rangle$ [a,d,e]	−190.04	−186.27	−302.90
$\langle y^2 \rangle$	−87.62	−85.51	−88.50
$\langle x^2 \rangle$	−13.68	−12.21	−15.17

	Benzo[*c*]furan	Benzo[*c*]thiophen (*spd* + $3s^1$ basis)
μ/D	−1.485	−0.054
π_1	0.044	−0.285
π_2	−0.357	−0.261
π_3	−0.094	−0.439
π_4	−0.550	−0.478
π_5	1.738	0.169
π_6		2.343
Electronic component		
$\langle z^2 \rangle$	−182.98	−246.62
$\langle y \rangle$	−84.10	−91.16
$\langle x^2 \rangle$	−11.91	−13.61

[a] All molecules lie in the *yz* plane with *z* as C_2 symmetry axis, the heteroatom lies along the positive *z* cartesian direction. [b] Distance from the C(3a)–C(7a) bond, with the molecular orientation as in footnote *a*. This gives a strict comparison with the data from refs. 8 and 11. [c] The binding energy of orbital π_i increases with an increase in *i*. [d] In units of 10^{-16} cm^2 (*cf.* ref. 8). [e] Values for benzene and naphthalene using the same orientation of the molecules are: benzene, −8.40 (π), −60.87 (σ), −60.87 (σ); naphthalene −13.59 (π), −107.47 (σ), −239.85 (σ).

from the monocyclic and Kekulé bicyclic compounds for comparison (with Table 1) are as follows: benzene, 212; pyrrole, 149; furan, 89; thiophen, 124 (*sp*-basis), 144 (*spd* + $3s^1$ basis); indene, 225; indole 308; benzo[*b*]-furan 232; benzo[*b*]thiophen, 242 (*sp* basis), 283 (*spd* + $3s^1$ basis).

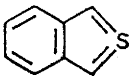
In the heterocycles (2a—c), the resonance energy is substantially lower than either naphthalene, the sum of the monocyclic heterocycles and benzene, or the corresponding Kekulé-like heterocycle. In the case of benzo-[*c*]furan the resonance energy is even lower than benzene itself. None the less the values are all significant in magnitude and as will be seen below this is consistent with their ^{1}H n.m.r. spectra which do not show purely polyolefinic character. It is worth noting in passing that some Hückel [23] and semi-empirical calculations [21,24] lead to substantially lower values for the resonance energy of (2a—c); however in this other work there is a change of definition of resonance energy. We have adopted the original one, namely that the resonance energy is the difference between the molecular total energy and the sum of the non-interacting bonds. In these other calculations, following Dewar *et al.*, the reference non-aromatic structure with zero resonance energy is defined as the corresponding acyclic polyolefin.

TABLE 5

Charge density at the nuclei and population analyses

Isoindole	N(2)	C(1)	C(3a)	C(4)	C(5)	H(1)	H(4)	H(5)	H(2)		
Charge density	190.241	116.746	116.722	116.760	116.771	0.355	0.364	0.364	0.368		
Population σ	5.8691	4.9093	4.9880	5.1390	5.1362	0.8498	0.8569	0.8576	0.6570		
π	1.5522	1.1261	1.0725	1.0017	1.0236						
Total	7.4216	6.0354	6.0605	6.1407	6.1598	0.8498	0.8569	0.8576	0.6570		
N-Methylisoindole	N(2)	C(1,3)	C(3a,7a)	C(4,7)	C(5,6)	C(Me)	H(1)	H(4)	H(5)	H(Me)(av)	$H(Me)_{ip}$
Charge density	190.315	116.758	116.724	116.760	116.770	116.732	0.356	0.364	0.365	0.372	0.370
Population σ	5.7864	4.8991	4.9888	5.1388	5.1351	5.1237	0.8532	0.8580	0.8587	0.4024	0.8217
π	1.5243	1.1336	1.0729	1.0027	1.0258	1.1647				0.4205	
Total	7.3107	6.0327	6.0617	6.1415	6.1609	6.2884	0.8532	0.8580	0.8587	0.8229	0.8217
Benzo[*c*]furan	O(2)	C(1)	C(3a)	C(4)	C(5)	H(1)	H(4)	H(5)			
Charge density	292.162	116.798	116.754	116.750	116.785	0.343	0.360	0.360			
Population σ	6.7716	4.8086	5.0073	5.1342	5.1406	0.8223	0.8477	0.8474			
π	1.7079	1.0090	1.0530	1.0009	1.0022						
Total	8.4795	5.8986	6.0603	6.1351	6.1488	0.8223	0.8477	0.8474			
Benzo[*c*]thiophen	S(2)	C(1)	C(3a)	C(4)	C(5)	H(1)	H(4)	H(5)			
Charge density	2 666.875	116.877	116.752	116.773	116.784	0.351	0.361	0.362			
Population σ	12.2349	5.0579	5.0062	5.1340	5.1450	0.8374	0.8511	0.8511			
π	3.7082	1.1016	1.0027	1.0027	1.0073						
Total	15.9430	6.1595	6.1366	6.1366	6.1523	0.8374	0.8511	0.8511			

We have commented previously that the $3d_S$ orbitals appear to fill the role of polarisation functions rather than strongly bonding orbitals in various formally covalent compounds; that is, the orbitals offer additional variational flexibility and have a refining role rather than changing the nature of the existing bonds. For benzo-[*c*]thiophen this is also apparent, indeed $3d_S$ orbital addition lowers the molecular energy by 0.118 45 a.u. marginally less than in the benzothiophen (0.124 03 a.u.). In view of the quinonoid form of the former, an increased $3d_S$ participation might have been expected had the $3d_S$ orbitals been important in the bonding for they offer an additional mode of delocalisation often expressed as



(13)

in (13). Only in the indene–2*H*-indene pair is a tautomeric equilibrium possible and the predicted energy difference favouring the Kekulé type is 153 kJ mol^{-1}. Few derivatives of the 2*H*-indene series are known, and those that have been obtained are (a) 2,2-disubstituted [25] and (b) unstable [26] in the absence of metal complexing agents, *e.g.* $Fe_2(CO)_9$.

Triplet States.—In the light of the significant amount of resonance energy still evident in (2a—c) we have investigated low lying triplet states to determine whether the instability of the compounds arises partly from low resonance energy and partly from a low lying excited state.

There is no experimental data available for triplet excitation in (2a—e), hence we also record data (Table 2) for the Kekulé-like series (1) where some experimental values are known.* In all cases, the triplet state is from the highest occupied π-level (HOMO) to the lowest unoccupied π-level (LUMO); in the quinonoid series this corresponds to the transition $a_2 \rightarrow b_1$, and in naphthalene $1a_u \rightarrow 2b_{2g}$. Comparison with the experimental data

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* Using the same geometric parameters to those of the LCGO calculations, we also calculated the triplet excitation energies by the semi-empirical INDO procedure (Table 2). Although the method also shows lower values for the quinonoid than the Kekulé forms, the difference between the two series is much smaller, and the special position of benzo[*c*]furan is not seen. It seems unlikely that the INDO method is satisfactory for excitation energies of this type.

[23] B. A. Hess, L. J. Schaad, and C. W. Holyoke, *Tetrahedron*, 1972, **28**, 3657, 5299; B. A. Hess and L. J. Schaad, *J. Amer. Chem. Soc.*, 1973, **95**, 3907.

[24] M. J. S. Dewar and N. Trinajstic, *Theor. Chim. Acta*, 1970, **17**, 235.

[25] W. R. Roth and J. D. Meier, *Tetrahedron Letters*, 1967, 2053.

[26] H. Tanida, T. Irie, and K. Tori, *Bull. Chem. Soc. Japan*, 1972, **45**, 1999.

for the Kekulé series shows that the present calculations reproduce the experimental values but are generally too large by *ca.* 0.5 eV in the UHF procedure. The calculated excitation energies in the quinonoid series are all substantially lower, and particularly so with 2*H*-indene and benzo[*c*]furan. This is consistent with the ready decomposition of benzo[*c*]furan at room temperature, even in an evacuated system, and in the absence of air.

The Molecular Orbital Energy Levels.—Detailed analysis of the form of the MO wave functions showed that there is a marked similarity in type of orbital both through the series (2a—e) and also with naphthalene. The comparatively few cross-overs in energy between orbitals from (2a—c and e) (Figure 2) can be ascribed to differences in the free atom orbital energies of the group X in (2); relevant figures (eV) at the Hartree–Fock limit[20] are: C, 2*s*: 19.20, 2*p*: 11.79; N, 2*s*: 25.72, 2*p*: 15.44; O, 2*s*: 33.86, 2*p*: 17.20; S, 3*s*: 23.94, 3*p*: 11.90 respectively. That there are so few cross-overs is surprising in view of the range of aromaticity, as evidenced by the resonance energies from naphthalene to 2*H*-indene; however, the majority of the orbitals are from the σ-system, and this is likely to be largely unchanged from aromaticity considerations. In fact the π-orbitals are quite variable in position in (2a—c) and (3). As with the monocyclic heterocycles (4), no degeneracy of the π- (or indeed σ-) levels is required by symmetry, but we have noted[27] that the separation of the two lowest binding energy π-levels [*e.g.* $2b_1$ and $1a_2$ in (4; X = O or NH)] varies in an order similar to the resonance energy sequence for [4; X = PH (planar), O, NH, or S] and being nearly degenerate in the most aromatic cases; the same effect occurs in the six-membered azines.[9] In the present molecules (2a—c and e) the highest occupied pair of levels follow the same trend, the separations being in the order 2*H*-indene > benzo[*c*]furan > isoindole > benzo[*c*]thiophen > naphthalene. A consequence of degeneracy of energy levels is frequently an even (highly symmetrical) electron distribution, as for example in the cyclic system C_nH_n. We return to the question of aromatic character in this series of molecules in the electron distribution and n.m.r. spectral sections below.

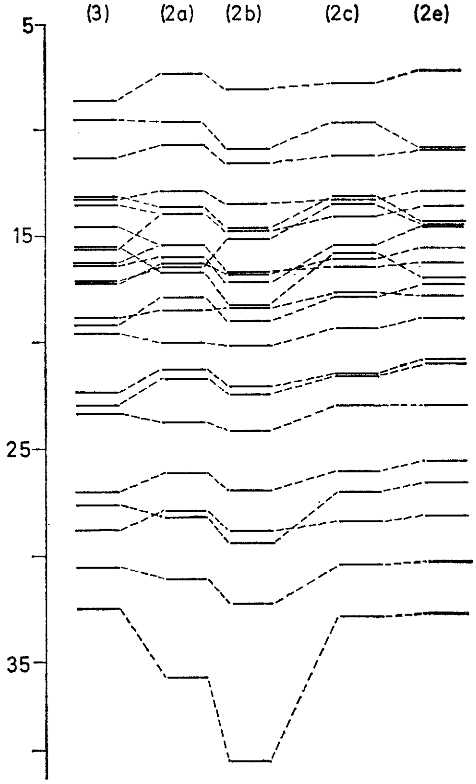


FIGURE 2 Correlation of the molecular orbital energy levels of isoindole (2a), benzo[*c*]furan (2b), benzo[*c*]thiophen (2c), 2*H*-indene (2e) with naphthalene (3)

Photoelectron Spectra.—In earlier work[3,4,9-11] we observed that the basis set used for C, H, N, O, and S leads to linear correlations of the former $IP_{obs} = A\,IP_{calc} + B$ with *A ca.* 0.75 and *B ca.* 1—2 eV, when Koopmans' theorem is used to equate occupied orbital energies to ionisation potentials. It was not surprising therefore to obtain similar linear correlations for (2b—d) and (3) as follows (with standard deviations in slope, intercept, and overall in parentheses): naphthalene, $IP_{obs} = 0.755IP_{calc} + 1.703$ eV (0.014, 0.213, 0.190); benzo[*c*]furan, $IP_{obs} = 0.770IP_{calc} + 1.42$ eV (0.013, 0.204, 0.177); benzo[*c*]thiophen, $IP_{obs} = 0.785IP_{calc} + 1.341$ eV (0.238, 0.229); *N*-methylisoindole, $IP_{obs} = 0.786IP_{calc} + 1.321$ eV (0.017, 0.259, 0.238). In all cases the correlations were assisted by (a) previous experience with related molecules, (b) the 1 : 1 correspondence of experimental and calculated values at the low binding energy region, and (c) the similarity of the calculated levels for isoindole and its *N*-methyl derivative. The present calculations reproduce the correct order for the first three (π-electron) IPs for the molecules (2b—d) and (3) namely: $(IP_1)_{(2d)} < (IP_1)_{(2c)} < (IP_1)_{(2b)} < (IP_1)_{(3)} < (IP_2)_{(2d)} < (IP_2)_{(3)} = (IP_2)_{(2c)} < (IP_3)_{(2d)} = (IP_2)_{(2b)} < (IP_3)_{(2c)} = (IP_3)_{(3)} < (IP_3)_{(2b)}$, where the nomenclature $(IP_n)_{(X)}$ refers to the *n*th IP of (*X*). The first four IPs of each of the series thiophen, benzo[*b*]thiophen, and isobenzo[*c*]thiophen have been reported;[28] the present calculations correctly order these 12 IPs with the single exception of $(IP_3)_{C_4H_4S}$ and $(IP_4)_{2O}$ which are reversed in order.†

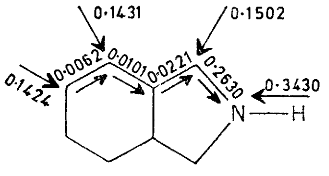
† The extended Hückel,[28] PPP,[22,28] and other [21] semi-empirical methods also lead to satisfactory correlations of the first three IPs, but the scatter is generally rather larger. There is also some ambiguity in the calculated data from ref. 28, where for both EHM and PPP calculations the text refers to considerably different correlation lines for the calculated and experimental IPs to those recorded in the caption to Figures 3 and 4 of ref. 28. It is of course possible that the calculations whilst reproducing the order correctly, do not attribute the correct symmetry type to each ionisation. At present there are few reliable ways of assigning the symmetry type experimentally beyond a σ–π separation, and we feel that the substantial agreement between the various calculations (refs. 21, 22, 28, and this paper) is self supporting in all cases except where very closely spaced IPs are concerned.

[27] M. H. Palmer and R. H. Findlay, *J.C.S. Perkin II*, 1975, 974.

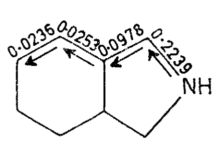
[28] P. A. Clark, R. Gleiter, and E. Heilbronner, *Tetrahedron*, 1973, **29**, 3087.

The Molecular Charge Distributions.—The experimental dipole moment for (2a—d) have not yet been reported, but the present work (Table 4) suggests that isoindole should be more polar than indole (calculated 2.31,[11] experimental 2.08 D), while benzo[*c*]furan and benzo[*c*]-thiophen should be less polar than either of the nitrogen compounds. Detailed analysis of the net atomic charges shows that much of the dipole moment in isoindole arises from the $N^{\delta-}-H^{\delta+}$ bond contribution, as in indole and pyrrole.[8]

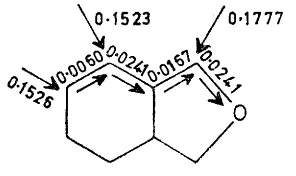
Population Analysis (*Table* 5).—As in the Kekulé series, the σ- and π-systems are polarised to the most distant part of the molecule (C-4, C-5), with the two systems operating in a compensating mode. In the *N*-methyl derivative, the CH_3 group is nearly neutral in the π-system (no hyperconjugative effect) but polarised towards nitrogen in the σ-system[(14)—(21)].



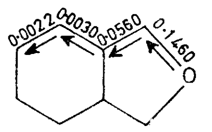
(14) (σ)



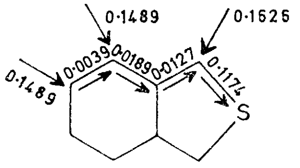
(15) (π)



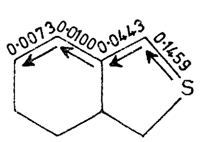
(16) (σ)



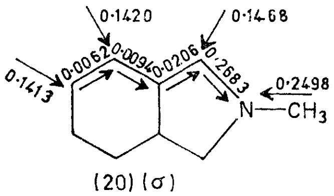
(17) (π)



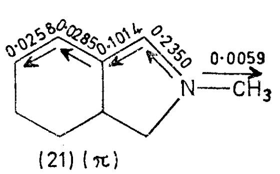
(18) (σ)



(19) (π)



(20) (σ)



(21) (π)

In the triplet states the heteroatom X in (2) receives additional population relative to the ground states for all cases (X = NH, O, or S); in view of the π-electron open-shell character of these triplet states it is not surprising that this arises primarily through the π-system, such that the heteroatom is a much weaker donor in the triplet state. However, detailed analysis of the π-MOs shows that very considerable reorganisation of the π-density occurs on formation of the triplet state; thus almost all the π-density at C-1 and -3 arises from the two single occupied orbitals rather than the double occupied ones. This is not at all evident from the small changes in total population.

Second Moments.—We have shown that the calculated second moments of the electronic charge distribution for a range of heterocycles are close to values obtained from microwave spectroscopy.[8] Again experimental values are awaited for (2a—d) and (3), but we report the calculated values here (Table 4).

The values for the π-system (*x*-axis) are of direct interest, and show that the π-electrons are much more diffuse in (2a—e) and (3) than in benzene, and that there is a trend to lower values as the electronegativity of the heteroatom increases. This is in part a result of an increasing level of localisation, and in part a smaller $(2p_\pi)_X$ atomic orbital radius.

Average Position of the π-Electrons.—We noted earlier that aromatic character is associated with a high tendency towards group (sextet, decet, *etc.*) behaviour, as opposed to pairwise π-electron behaviour.[8,11,27] This group character is best achieved by (ideally) coincident average electronic positions $(\bar{x},\bar{y},\bar{z})$. For highly symmetrical hydrocarbons such as benzene this is automatically the case by symmetry and further development of the concept is required to distinguish between say benzene and naphthalene aromatic character in this way. However, for the heterocycles (2a—d) this problem does not arise (Table 4), and we record the average position of the π electrons along the C_2 symmetry (*z*-axis) with C(3a)—(7a) (*y*-axis) as origin. This enables direct comparison with both the monocyclic[8] and Kekulé bicyclic[11,27] systems reported previously. It is appropriate to omit the core π-electron $(2p_x)_s$ orbital (π_6) from the analysis, and also to omit the antisymmetric CH bonding level (π_6) of the CH_2 group in (2d). The remaining spread of values (Å) varies from naphthalene (0.0), through benzo[*c*]thiophen (0.76), isoindole (2.12), benzo[*c*]furan to 2*H*-indene (2.49 Å), a sequence again parallel to qualitative views of aromatic character, except for a possible inversion of order in (2a and c). Comparison with the Kekulé series is not straightforward owing to the non-coaxial character of the mean positions in the latter series.

^{1}H *N.m.r. Spectra of* (2b—d).—The relative values of the vicinal coupling constants in adjacent bonds of carbocyclic systems have been widely used as a measure of relative bond orders[29] and through them relative levels of aromatic character.[30-32]

As was mentioned above, the molecules (2b—d) show six-spin coupled spectra, and these were analysed by an initial AA^1BB^1 analysis of the 4—7-H portion, followed by a full 6-spin analysis after a series of non-iterative computations established acceptable estimates for the inter-ring

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[29] M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 1969, **91**, 6325.

[30] H. Sofer and O. E. Polansky, *Monatsh.*, 1971, **102**, 256.

[31] J. D. White, M. E. Mann, H. D. Kirshenbaum, and A. Mitra, *J. Org. Chem.*, 1971, **36**, 1048.

[32] P. Crews, R. P. Kintner, and H. C. Padgett, *J. Org. Chem.*, 1973, **38**, 4391.

coupling constants. The final results of the $AA^1BB^1CC^1$ spectra yielded root mean square deviations of the transition frequencies around 0.1 Hz, and standard deviations in the coupling constants (Table 6) of *ca.* 0.05 (2b and c) and 0.04 Hz (2d). The values of the vicinal coupling constants $J_{4,5}$ and $J_{5,6}$ in *N*-methylisoindole (Table 6) are very similar to those of the 1,3-diphenyl derivative ($J_{4,5}$ 8.63, $J_{5,6}$ 6.39 Hz) cited above;[32] furthermore, the near constancy[32] of the average vicinal coupling $J_{av} = 0.5\ (J_{4,5} + J_{5,6})$ of *ca.* 7.5 Hz can be extended to (2b—d). The ratio $J_{4,5} : J_{5,6}$ is nearly constant for the latter trio (0.70, 0.72, 0.74 respectively), and lies in the expected position based upon aromatic character considerations, relevant figures for the ratio being: benzene (1.00), naphthalene (0.82),[29,33] and cyclohexa-1,3-diene (0.52).[29] However, extension of the concept to bicyclic systems having lower than D_{2h} symmetry brings certain problems, especially in the heterocyclic field; for example (a) there may be more than one pair of unique vicinal couplings and (b) the ratio may not yield information for the overall aromatic character, but merely for the one ring under consideration. The Kekulé bicyclic heterocycles (1) exemplify both these difficulties since $J_{4,5} \neq J_{6,7}$; if the former is chosen, by virtue of being further removed from the heteroatom, the ratios $J_{4,5} : J_{5,6}$ are 0.90 (1; X = NH),[34] 0.93 (1; X = O),[35] and 0.89 (1; X = S).[34] Both thermochemical data, and our earlier calculations,[11] suggest that the series (1; X = NH, O, and S) are less aromatic than naphthalene but more aromatic than benzene *overall*, *i.e.* have lower and higher resonance energies than these two reference compounds respectively. This anomaly, the resonance energy and coupling constant ratio indicating opposite aromatic character relative to naphthalene can be reconciled, if it is assumed that almost all the resonance energy in the Kekulé systems (1) is restricted to the carbocyclic ring; under these conditions the coupling constant ratio is expected to be near to that of benzene.

TABLE 6

^{1}H N.m.r. parameters

(*a*) ^{1}H Shifts	ν_1	ν_4	ν_5
Benzo[*c*]furan[a] (i)	−798.90	−738.07	−683.90
(standard deviation)	(0.024)	(0.027)	(0.030)
Benzo[*c*]thiophen[b]	−763.40	−759.30	−704.16
(standard deviation)	(0.036)	(0.032)	(0.034)

(*a*) H Shifts	ν_1	ν_4	ν_5
N-Methylisoindole[c]	−704.54	−751.21	−691.72
(standard deviation)	(0.019)	(0.022)	(0.023)

	ν_1	ν_2
Naphthalene	−782.0[d]	−745.7[d]

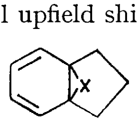
	ν_1	ν_2
Cyclohexa-1,3-diene[f]	−568.31[g]	−582.89[g]

(*b*) ^{1}H Couplings	$J_{1,3}$	$J_{1,4}$	$J_{1,5}$	$J_{1,6}$	$J_{1,7}$	$J_{4,5}$	$J_{4,6}$	$J_{4,7}$	$J_{5,6}$
Benzo[*c*]furan[a]	−0.001	0.637	0.039	0.044	0.014	0.852	1.008	0.570	6.223
(standard deviation)	(0.035)	(0.039)	(0.046)	(0.046)	(0.039)	(0.049)	(0.048)	(0.40)	(0.048)
Benzo[*c*]thiophen[b]	0.017	0.422	0.030	−0.139	−0.086	0.864	1.030	0.785	6.356
(standard deviation)	(0.040)	(0.056)	(0.068)	(0.071)	(0.058)	(0.056)	(0.057)	(0.048)	(0.060)
N-Methylisoindole[c]	0.0	0.457	0.070	−0.070	−0.081	8.690	0.899	0.790	6.456
(standard deviation)	(0.040)	(0.035)	(0.042)	(0.042)	(0.035)	(0.039)	(0.039)	(0.034)	(0.039)

	$J_{1,5}$	$J_{1,6}$	$J_{1,7}$	$J_{1,8}$	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$
Naphthalene	0.85[e]	−0.10[e]	0.23[e]	−0.45[e]	8.28[e]	1.24[c]	0.74[e]	6.85[e]
Cyclohexa-1,3-diene[f]					9.64	1.02	1.12	5.04
					9.55	0.89	0.88	5.35

[a] Concentration 7.7 g l^{-1} in $CDCl_3$ (273 K), under N_2, $AA^1BB^1CC^1$ analysis. [b] Concentration 7.3 g l^{-1} in $CDCl_3$ (253 K), under N_2, $AA^1BB^1CC^1$ analysis. [c] Concentration 16 g l^{-1} in $CDCl_3$ (273 K), under N_2, $AA^1BB^1CC^1$ analysis. [d] Concentration 15 g l^{-1} in $CDCl_3$ (273 K), AA^1BB^1 analysis. [e] R. W. Crecely and J. H. Goldstein, *Org. Magnetic Resonance*, 1970, **2**, 613. [f] M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 1969, **91**, 6325. [g] In C_6H_6.

Finally we briefly report that the ^{13}C n.m.r. spectrum of (2d) yields chemical shifts as follows: CH_3: 37.34; C-1 and -3: 111.50; C-4 and -7: 119.22; C-5 and -6: 120.30; C-3a and -7a: 124.00 p.p.m. respectively. The carbocyclic C_α (4,7) and C_β(5,6) shifts are very similar, and the assignment order was confirmed by off-resonance proton decoupling (above). The C_α, C_β shifts of naphthalene (128.3; 126.1),[36] indole (C-4, 121.3; C-5, 122.3),[37] indane (124.0, 125.9),[38] other aromatic bicyclic compounds,[38] and non-aromatic congugated compounds are similar [(22a), 119.2; (22b), 128.3, 126.3 p.p.m. respectively].[39] The most consistent feature of the *N*-methylisoindole spectrum is the general upfield shift relative to most of the above by *ca.* 6 p.p.m. for the carbocyclic carbon atom, while the C-1 and -3 resonances are even further upfield than C-2 of pyrrole (118.7) or indole (125.2).[37] Whether this can be ascribed to a ring current effect remains to be determined.



(22) a; X = CH_2

Conclusions.—There seems little doubt that the quinonoid heterocycles (2) still retain some resonance energy (RE) in the ground state; however, the numerical values

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are low, and as long suspected, well below that of the Kekulé series (1). The lack of stability of the molecules is readily attributed to the low RE and to the low lying triplet state. The photoelectron spectra of (2b—d) are satisfactorily interpreted by the present calculations; the molecular orbitals are very similar to corresponding ones in naphthalene, but the π-levels disclose substantial shifts in energy between orbitals of similar symmetry across the series (2b—d) and (3). As a consequence of this the electron distributions and degree of electron delocalisation as evidenced by group behaviour is rather variable.

The ^{1}H n.m.r. spectra of (2b—d) show strong alteration in magnitude of the vicinal coupling constants, and the ratio again suggests low aromatic character; however, the extension of this concept to heterocycles generally brings major difficulties, unless the aromatic considerations are restricted to individual rings, rather than overall aromaticity.

We are grateful to the S.R.C. and to the Director of the Atlas Laboratory for the provisions of computational facilities and for a grant to S. M. F. K.

[5/413 *Received, 28th February,* 1975]