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THEORETICAL STUDIES OF POSITIONAL ISOMERS OBTAINED BY ANNELATION OF BENZENE AND 5-MEMBERED RING HETEROCYCLICS CONTAINING NITROGEN, OXYGEN, OR SULPHUR†

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Abstract—MO calculations using the Pariser–Parr approach are reported for the "normal" heteroaromatic molecules: indole, benzofuran, and thionaphthene, and for their isoconjugated isomers: isoindole, isobenzofuran, and isothionaphthene. The agreement between the observed and calculated transition energies is satisfactory. The reactive positions towards electrophilic, nucleophilic, and radical attacks are predicted. Recently made benzo[e]isoindole is also studied.

INTRODUCTION

THE annelation of benzene and conjugated 5-membered heterocyclic molecules containing a single heteroatom (e.g., pyrrole, furan, thiophene) leads to bicyclic molecules, isoelectronic with naphthalene, which fall distinctly in two classes depending on where the annelation on the 5-membered ring occurs. If the annelation happens at the short (2,3) bond the resulting compounds belong to the so-called "normal" series[1]: indole (**1**), benzofuran (**3**), and thionaphthene (**5**). But, if the annelation occurs at the long (3,4) bond of the 5-membered ring the resulting compounds belong to the isoconjugated isomers series[1]: isoindole (**2**), isobenzofuran (**4**), and isothionaphthene (**6**). These two classes of molecules differ considerably in their properties and structures. We denote the isomeric pairs—indole: isoindole, benzofuran: isobenzofuran, and thionaphthene: isothionaphthene—as positional isomers[2,3], because they formally differ only in the position of the heteroatom.

"Normal" molecules **1**, **3**, and **5** are stable, chemically well defined species, and were first prepared[4] many years ago. Their isoconjugated isomers **2**, **4**, and **6** are only recently made[5] after almost a century of unsuccessful attempts.[6] These are highly reactive species. Theoretical studies[1,2] within the Dewar's variant[7] of the SCF MO procedure of Pople[8] predicted indole, benzofuran, and thionaphthene to be aromatic molecules with the index of aromatic stabilization (A_s)[2]: (**1**) = 23·8 kcal/mol[1]; (**3**) = 20·3 kcal/mole[1]; and (**5**) = 24·8 kcal/mole.[8] On the other hand, isoconjugated isomers isoindole, isobenzofuran, and isothionaphthene are predicted to be less stable: A_s values being: (**2**) = 11·6 kcal/mole[1]; (**4**) = 2·4 kcal/

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mole[1]; and (**6**) = 9·3 kcal/mole,[9] and structurally very different from "normal" molecules. While in the "normal" heteroaromatic molecules the benzene moiety preserved benzene structure with all bonds about 1·40 Å, the isoconjugated molecules have polyenoid structure with C—C bonds strongly alternating between 1·35 Å and 1·46 Å. Such a structural arrangement makes molecules **2**, **4** and **6** very active in the Diels–Alder sense. For example, isothionaphthene, unlike thionaphthene, undergoes Diels–Alder addition of maleic anhydride.[10]

In this communication we wish to report our studies on the electronic spectra of of the positional isomers, which atomic skeletal structures are presented in Fig 1.

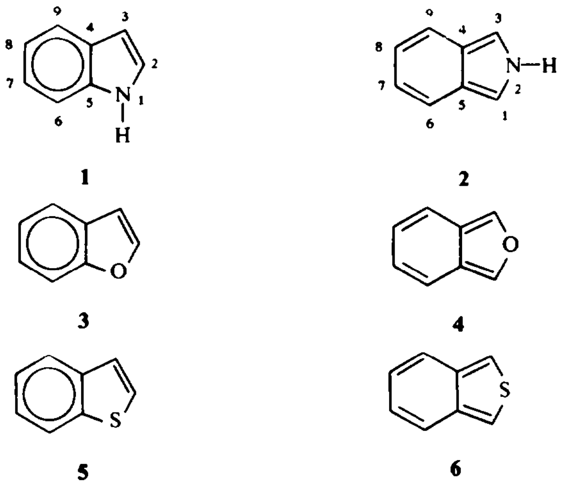


Fig 1. Atomic skeletal structures of the studied pairs of positional isomers [indole(**1**): isoindole(**2**): benzofuran(**3**): isobenzofuran(**4**): thionaphthene(**5**): isothionaphthene(**6**)]

Method of calculation and parameters

In the present work we have used the semiempirical SCF MO method of Pariser and Parr[11,12] (P–P method), which has been shown to be very reliable for studying the electronic spectra of various kinds of conjugated molecules.[12–14] Since the formalism of P–P method is well known and has been presented rather extensively in recent monographs[12–14] it need not to be repeated here.

All electronic repulsion integrals have been treated semiempirically. For the one-centre repulsion integrals the values proposed by Billingsley and Bloor[15] were adopted. The two-center repulsion integrals were determined in the Mataga–Nishimoto manner.[16]

The values of Billingsley and Bloor[15] for one-electron core resonance integrals $\beta_{C—B}$ (X being N, O, or S) have been used.

For $\beta_{C—C}$ the value recommended by Pariser and Parr[11] was adopted. The parameter set used is listed in Table 1.

In the present calculations sulphur is considered without d-orbital participation. There are several reasons for this: the experience of various authors in their studies,[17] our recent works on the ground and excited states of sulphur compounds,[3,18] and finally some recent ab initio SCF MO calculations on very small sulphur molecules

$(H_2S)^{19}$ or ions (α-sulphinyl carbanion)[20] have shown negligible d-orbital participation.

Apparently the 3d AO's of bivalent sulphur are too high in energy to have much importance in bonding.[21] It is true that the contrary opinions have been expressed on the basis of semi-empirical calculations;[22] here, however, the role of 3d AO's depends on the choice of parameters.

All calculations have been carried out with a Fortran program coded for a CEA 90–40 computer.

RESULTS AND DISCUSSIONS

In the past there was a number of theoretical investigations using various parametrization schemes on the electronic spectra of indole, benzofuran, and thionaphthene giving in most cases a reasonably good agreement with experimental data.[15, 23, 24] On the other hand, there were very few theoretical investigations[24] of isoindole, isobenzofuran, or isothionaphthene. So far, there was no theoretical study undertaken simultaneously for all these molecules with the same set of approximations in order to compare their spectral data. Here we present our attempt in this respect.

We report the calculated and experimental singlet–singlet transition energies (ΔE, eV), experimental intensities (log ε), and oscillator strengths (f) in Table 2. The electronic transition energies and oscillator strengths have been calculated by a limited configuration interaction (LCI) procedure. In Table 2 we also give the weights (in %) of the most important configurations in LCI procedure.

The agreement between the experimental and calculated values is very good indeed. The slope of the least-squares line (0·986) is nearly equal to the theoretical value of unity; the correlation coefficient being 0·99 and the standard deviation only 0·026 eV. (see Fig. 2).

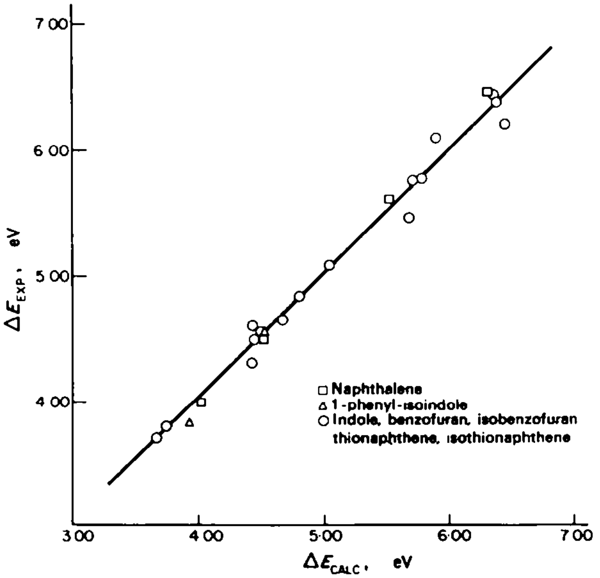


FIG 2. Plot of calculated vs. observed lower singlet–singlet transition energies of the studied positional isomers.

It is interesting that UV spectrum of 1-phenyl-isoindole[21] is closely reproduced by our calculation for isoindole. Apparently, this is a case where the conjugative effect of the phenyl ring is overbalanced by steric repulsions. Calculated length of the bond between the phenyl ring and C_1-atom of isoindole is rather long (1·465 Å) when compared with standard aromatic carbon–carbon bond length ($\sim$1·40 Å). A similar result was observed in other molecules where two heterocyclic ring systems were separated by one C—C bond.[26]

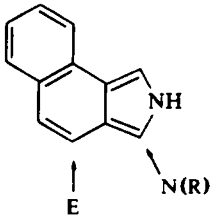
In connection with the P—P calculations reported here concerning π—π^* transitions in the studied molecules, it would be interesting to find out the role of nonbonding electrons in these transitions. The required information could be obtained by means of an SCF method which includes all valence electrons explicitly in the treatment. Such a method is, for example, the well known CNDO/2 method of Pople, Santry, and Segal,[27] which in the original form is not suitable for predicting correct transition energies. CNDO/2 method was adopted for spectroscopic calculations by Del Bene and Jaffè.[28] The transition energies thus obtained can then be refined by a configuration interaction procedure.

In the present work we applied this so-called CNDO-C I method to benzofuran, which we have chosen as model molecule for studying the effect of nonbonding electrons. We used the original parametrization scheme[28] and in the CI procedure we have included 50 lowest configurations.

The CNDO–CI procedure gave that the highest three occupied and lowest four empty MO's are π-orbitals. The next two occupied MO's are σ-orbitals which contain, in part, the nonbonding electrons of oxygen. The obtained results are presented in Table 3.

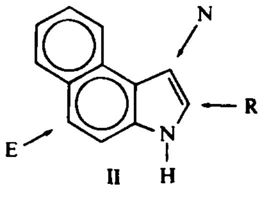
The agreement with experiment is not so good as was obtained with the P–P approach. But, CNDO–CI calculations indicated that in the lower transitions one is due to the transition of the nonbonding electron on oxygen to virtual π orbital. This transition is not observed experimentally because of its much lower intensity, thus being hidden by the much more intense π–π^* bands.

We have also studied recently prepared[29] benz[*e*]isoindole



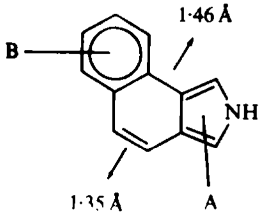
I

In our recent paper[1] we predicted this molecule to be relatively stable, A_s being only 6 kcal/mole less than that of the isomeric benz[f]indole prepared many years ago.[30]



II

Benz[e]isoindole can be regarded as 3-phenylindole in which a localized ethylene bridge (~1·35 Å) connects two ring systems.



It was found earlier[31] that if the aromatic component A is linked together with the aromatic component B through an essential single bond (~ 1·46 Å) the A_s value of the parent compound can be estimated rather accurately from the A_s values of the components:

$$A_s(A—B) \simeq A_s(A) + A_s(B)$$

The difference between the calculated A_s value of benz(e)isoindole using Dewar's approach[7] (30·0 kcal/mole) and the above expression (28·4 kcal/mole) is negligible (1·6 kcal/mole). This consideration, of course, supports the idea that the double bond in the position 6,7 is localized.

We have reproduced the electronic spectrum of benz[e]isoindole quite well. Results for the lower transition energies are as follows (experimental values[30] are in brackets): 3·38 eV; 3·79 eV (3·63 eV); 4·27 eV (4·23 eV); 4·79 eV; and 5·31 eV (5·10 eV).

Finally, we report π-electron densities in Table 4, and bond orders in Table 5. Charge densities can be used within the isolated-molecule approximation[32] for predicting the most reactive positions on the each studied molecule. This is, of course, a very approximate approach but useful for qualitative predictions.[33] Using this approach we predict positions 3 (indole, benzofuran, and thionaphthene) and 1 (isoindole, isobenzofuran, and isothionaphthene) to be the most reactive towards the attack of electrophilic reagents. Similarly, the positions 9 (indole, benzofuran, and thionaphthene) and 6 (isoindole, isobenzofuran, and isothionaphthene) are predicted to be the most reactive sites for nucleophilic attack. Addition reactions will most probably happen at bonds with the highest values of bond order. Thus, we predict the following bonds to be the most reactive: 2–3 (indole, benzofuran, and thionaphthene) and 6–7 (isoindole, isobenzofuran, and isothionaphthene).

The most reactive positions towards radical attack were obtained by considering the free valence indices (Table 6). On these grounds we predicted positions 2 (indole, benzofuran, and thionaphthene) and 1 (isoindole, isobenzofuran, and isothionaphthene) to be the most reactive sites for radical attack. The most reactive positions predicted on benz[e]isoindole(I) and benz[f]indole(II) towards electrophilic (E), nucleophilic (N), or radical (R) attacks are indicated.

TABLE 1. VALUES OF THE PARAMETERS USED IN THE CALCULATIONS

Atom (×)	Valence State	W_x(eV)	γ_{xx}(eV)[a]	β_{C-X}(eV)[a,b]	r_{C-X}(Å)[c]
C	trtrtr π	11·16	11·13	−2·390	1·400
N	trtrtr π^2 (>N—)	24·80	16·76	−1·800	1·380
O	tr^2trtr π^2 (>O)	33·00	21·53	−1·800	1·370
S	tr^2trtr π^2 (>S)	22·20	13·05	−1·500	1·720

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TABLE 2. CALCULATED AND EXPERIMENTAL SINGLET–SINGLET TRANSITION ENERGIES, EXPERIMENTAL INTENSITIES (LOG ε), OSCILLATOR STRENGTHS (f), AND WEIGHTS (IN %) OF MOST IMPORTANT CONFIGURATIONS

Molecule	Transition energies (eV)				Weight of configurations	
	Experimental	log ε	Calculated	f		
Indole	4·49[a]	3·71	4·45	0·08	$\phi_4^6 ; \phi_5^6$	33; 32
	4·65	3·80	4·67	0·12	ϕ_5^6	54
	5·76	4·35	5·71	1·05	$\phi_5^7 ; \phi_4^6$	47; 43
			6·16	0·12	$\phi_4^7 ; \phi_3^6$	42; 32
	6·38	4·35	6·38	0·33	ϕ_5^8	74
			6·56	0·50	$\phi_3^6 ; \phi_4^7$	48; 35
			6·77	0·08	$\phi_3^7 ; \phi_4^8$	36; 26
Isoindole	3·82[b]	2·99	3·93	0·33	ϕ_5^6	96
	4·56	2·86	4·54	0·01	$\phi_4^6 ; \phi_5^7$	54; 42
			5·41	0·02	ϕ_5^8	78
			5·92	0·0001	ϕ_3^6	77
			6·10	1·86	$\phi_5^7 ; \phi_4^6$	55; 43
			6·48	0·01	ϕ_4^8	61
Benzofuran	4·52[a,c]	3·40	4·55	0·004	$\phi_4^6 ; \phi_5^7$	50; 44
	5·08	4·00	5·05	0·48	ϕ_5^6	91
	6·10	4·35	5·91	0·64	$\phi_5^7 ; \phi_4^6$	51; 40
			6·36	0·13	ϕ_3^6	44
	6·45	4·10	6·56	0·53	ϕ_4^7	55
			6·79	0·11	ϕ_4^8	44
Isobenzofuran	3·80[b]		3·75	0·37	ϕ_5^6	98
			4·57	0·002	$\phi_4^6 ; \phi_5^7$	51; 46
			5·17	0·01	ϕ_5^8	65
			5·74	0·01	ϕ_3^6	64
			6·18	1·87	$\phi_5^7 ; \phi_4^6$	52; 47
			6·64	0·002	$\phi_4^8 ; \phi_3^7$	47; 31
Thionaphthene	4·31[a,c]	3·31	4·43	0·07	$\phi_4^6 ; \phi_5^7$	37; 29
	4·83	3·74	4·81	0·31	ϕ_5^6	68
	5·46	4·45	5·68	0·91	$\phi_5^7 ; \phi_4^6$	51; 40
			5·86	0·17	$\phi_4^7 ; \phi_3^6$	45; 32
	6·20	4·35	6·45	0·43	$\phi_3^6 : \phi_4^7$	47; 28
			6·54	0·30	ϕ_5^8	65
			6·73	0·09	ϕ_3^7	48

TABLE 2 – *continued*

Molecule	Transition energies (eV)				Weight of configurations	
	Experimental	log ε	Calculated	f		
Isothionaphthene	3·78[e, f]	3·13	3·67	0·38	ϕ_5^6	95
	4·46	3·34	4·44	0·06	ϕ_4^6	62
			5·07	0·02	ϕ_5^8	65
			5·71	0·02	ϕ_3^6	66
	5·79	4·84	5·79	1·60	ϕ_5^7; ϕ_4^6	55; 35
			6·45	0·19	ϕ_4^8	47
			6·98	0·05	ϕ_2^6	71

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TABLE 3. CNDO–CI RESULTS FOR THE LOWER TRANSITION ENERGIES IN BENZOFURAN

E (eV)	f	Character of the transition	Transition
4·25	0·018	$\pi - \pi^*$	2,1′ (+4,1′)
4·45	0·079	$\pi - \pi^*$	1,1′ (−4,1′)
5·52	0·137	$\pi - \pi^*$	2,1′ + 1,2′ − 1,1′ (−4,1′)
6·03	0·000	$\sigma(n) - \pi^*$	4,2′
6·17	0·120	$\pi - \pi^*$	1,2′
6·27	0·387	$\pi - \pi^*$	2,2′

TABLE 4. π—ELECTRON DENSITIES

(a) "Normal" Compounds

Molecule	1	2	3	4	5	6	7	8	9
Indole	1·6444	1·0863	1·0893	1·0385	1·0746	1·0359	1·0110	1·0195	0·9998
Benzofuran	1·8246	1·0320	1·0532	1·0235	1·0264	1·0254	1·0040	1·0115	0·9995
Thionaphthene	1·7874	1·0421	1·0613	1·0249	1·0327	1·0253	1·0091	1·0153	1·0019

(b) Isoconjugated Isomers

Molecule	1	2	4	6	7
Isoindole	1·1553	1·5380	1·0468	1·0107	1·0182
Isobenzofuran	1·0724	1·7585	1·0333	1·0048	1·0102
Isothionaphthene	1·0913	1·6931	1·0378	1·0078	1·0167

TABLE 5. BOND ORDERS

(a) "Normal" Compounds

Molecule	1–2	2–3	3–4	4–5	5–6	6–7	7–8	8–9
Indole	0·4731	0·8035	0·4820	0·5719	0·5831	0·7166	0·6103	0·7223
Benzofuran	0·3407	0·8637	0·4330	0·6004	0·6157	0·6971	0·6296	0·7066
Thionaphthene	0·3723	0·8580	0·4304	0·5954	0·6180	0·6960	0·6299	0·7049

(b) Isoconjugated isomers

Molecule	1–2	3–4	4–5	5–6	6–7	7–8
Isoindole	0·5404	0·6482	0·4894	0·4920	0·7722	0·5499
Isobenzofuran	0·4123	0·7102	0·4562	0·4659	0·7889	0·5289
Isothionaphthene	0·4532	0·7094	0·4477	0·4684	0·7872	0·5288

TABLE 6. FREE VALENCE INDICES*

(a) "Normal" Compounds

Molecule	2	3	6	7
Indole	0·1374	0·1285	0·1161	0·0871
Benzofuran	0·2096	0·1173	0·1012	0·0873
Thionaphthene	0·1837	0·1256	0·1000	0·0881

(b) Isoconjugated Compounds

Molecule	1	6	7
Isoindole	0·2254	0·1498	0·0819
Isobenzofuran	0·2815	0·1592	0·0962
Isothionaphthene	0·2514	0·1584	0·0980

* Free valence indices are calculated using for $N_{max} = \sqrt{2}$; a value which was suggested by Burkitt, Coulson and Longuet-Higgins (*Trans. Faraday Soc.* **47**, 553 (1951)) for secondary carbon atoms

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Note added in proof:

Recently, Bonnett and Brown (*Chem. Commun.*, 393 (1972)) prepared isoindole and found it to be very unstable: isoindole decomposes rather rapidly at room temperature. The electronic spectrum of isoindole was measured in degassed hexane and it shows vibrational fine structure (λ_{max} = 263·5, 268·5, 275, 286·5, 294, 300, 306·5, 312·5, 320, 326·5 and 335 nm). Our calculations predicted λ_{max} at 273 and 315 nm.