Some ab Initio Calculations on Indole, Isoindole, Benzofuran, and Isobenzofuran

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Ab initio calculations in the framework of the methodology of Pople et al. have been performed on indole, isoindole, benzofuran, and isobenzofuran. Several molecular properties (dipole moments, n. m. r. chemical shifts, stabilities, and reactivities) correlate well with calculated indices (charge densities, HOMO-LUMO separation). The calculations failed to give magnitudes of first ionization potentials, although the correct trends are reproduced, i. e. giving higher values to more stable isomers. Some of the obtained results (charge densities, dipole moments) parallel CNDO/2 values.

Introduction

Indole (1), benzofuran (3) and their isoconjugated isomers: isoindole (2) and isobenzofuran (4) are interesting heteroaromatic molecules[1–3] denoted as positional isomers[4] because they formally differ only in the position of a heteroatom. Their atomic skeletal structures and a numbering of atoms are given in Figure 1.

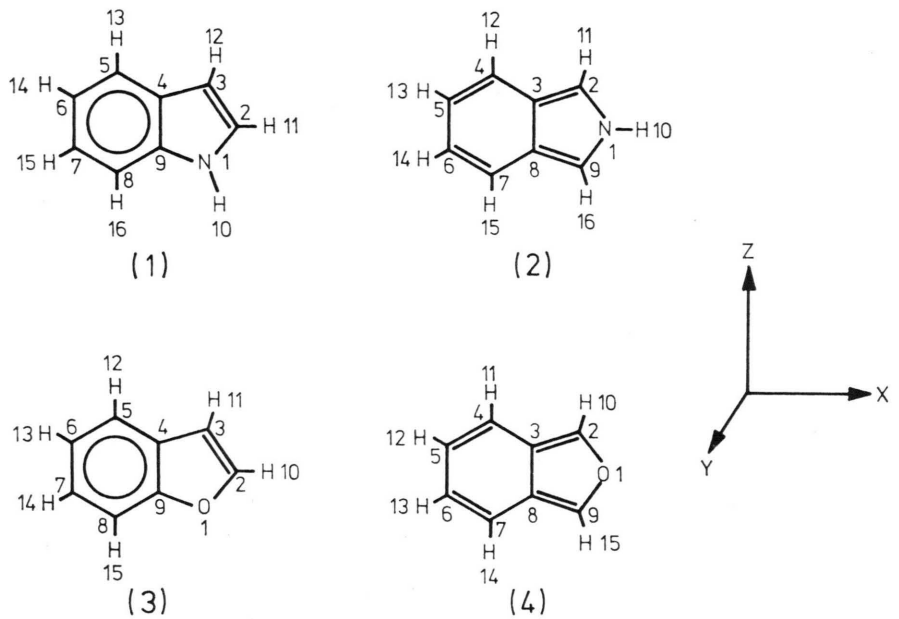

Fig. 1. Atomic skeletal structures and numbering of atoms for indole (1), isoindole (2), benzofuran (3), and isobenzofuran (4).

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The difference in the position of a heteroatom reflects rather strongly the differences in physical and chemical properties of positional isomers [4–6]. Theoretical studies [7] using the Dewar's variant [8] of the Pople's SCF MO [9] (variable β) [10] procedure predicted the geometries of 1, 2, 3, and 4, respectively. These results can be summarized as follows: the benzene ring in indole and benzofuran is unaffected by the attachment of the N- or O-polyenoid moiety whereas isoindole and isobenzofuran have a quinonoid structure, because in these molecules the six-membered ring has lost the benzene-like geometry becoming a cyclopolyenoid C_6 moiety. These quinonoid-like structures are very reactive in the case of $(4m+2)$-rings [11]. Thus, while 1 and 3 were first prepared a century ago [12–14] and possess a considerable aromatic stabilization [the DRE and REPE values [15] being (1) 23.8 kcal/mole, (3) 20.3 kcal/mole, (1) 0.047 β, and 0.036 β, respectively] [7, 16], 2 and 4 are of more recent date [6, 17–22] and possess a lower aromatic stabilization [the DRE and REPE values being (2) 11.6 kcal/mole, (4) 2.4 kcal/mole, (2) 0.029 β, and (4) 0.002 β, respectively] [7, 16].

Indole and benzofuran also appear as the fundamental constituent parts of many biologically active molecules [3, 23, 24], e.g.: indole-3-acetic acid (the natural plant growth hormone), tryptamine (the hallucinogenic agent), lysergic acid diethylamine (the most potent hallucinogen), serotonin (the effect on the blood vessels), indomethacin (the potent anti-inflammatory agent), medmain (the potent serotonin antagonist), 5-methoxy-6,7-dimethyl benzofuran (the aroma-constituent of greek tabacco), 2-methyl benzofuran (the aroma constituent of coffee), etc. Indole and benzofuran have been found in cigarette smoke [25] and tested on chemical carcinogenecity [26, 27] showing no carcinogenic activity. On the other hand, the corresponding isoconjugated isomers have never been detected to our knowledge as parts of biological molecules.

In the past, the theoretical studies [7, 16, 28–36] on 1, 2, 3, and 4 in their ground and excited states have been performed in the framework of the approximate molecular orbital methods. We have decided to study these molecules using an ab initio LCAO-SCF-MO approach and to compare our results with some previously obtained by semi-empirical methods.

Computational Details

Indole, isoindole, benzofuran, and isobenzofuran have been studied by an ab initio (Hartree-Fock-Roothaan) LCAO-SCF-MO procedure [37]. The main problem in ab initio calculations are, of course, the difficulties in the evaluation of the multicenter electron repulsion integrals over the Slater-type orbitals (STO). Several research workers [38–42] have shown that the difficulties of integral evaluation can be overcome by simulating each STO (Φ_μ) as a linear combination of K 1 s and 2 p Gaussian-type orbitals (GTO) $g_{\mu k}$:

$$\Phi_\mu = \sum_{k=1}^{K} c_{\mu k}\, g_{\mu k} .$$

Hehre, Stewart, and Pople [41] have optimized the GTO exponents (and have found that these do not depend on the size of the basis set) and have determined the expansion coefficients $c_{\mu k}$ by a least-squares fit of the STO's using expansions where K ranges from 2 to 6 (termed STO-K G expansions). Pople and co-workers [41, 42] have found in their studies that the three-gaussian representation (STO-3G) set is very economical to use (gives results – atomic population, dipole moments, barriers to rotation around the single bond – close to the STO limit) and as a minimal (1 s, 2 s, 2 p) basis can be applied to larger molecules. Therefore, following their experience the STO-3G basis functions have been also used in the present work.

The LCAO coefficients are obtained solving the Hartree-Fock-Roothaan equations. The Mulliken gross population [43] of the atomic orbital Φ_μ is calculated from the expression:

$$q_\mu = P_{\mu\mu} + \sum_{\nu(\neq\mu)} P_{\mu\nu} S_{\mu\nu}$$

where $P_{\mu\nu}$ is a first-order density matrix ($P_{\mu\nu} = 2 \sum_{i}^{\text{occ.}} c_{\mu i}\, c_{\nu i}$). The electric dipole moments are evaluated from the formula:

$$\boldsymbol{\mu}\,(\mathrm{D}) = 2.5416 \left\{ \sum_{A} Z_A \mathbf{r}_A - \sum P_{\mu\nu} \mathbf{r}_{\mu\nu} \right\}$$

where

$$\mathbf{r}_{\mu\nu} = \int \Phi_\mu \mathbf{r}\, \Phi_\nu \, \mathrm{d}V .$$

The geometries of studied molecules are needed for the input data. Unfortunately, the experimental geometries of indole, isoindole, benzofuran, and isobenzofuran are not known as yet. The experimental bond lengths in the 3-methylindole-trinitrobenzene complex [44] and the crystal structure of indole [45] are,

so far, determined only. Since these data [44, 45] are not very helpful for our purpose we have used the standard bond lengths as suggested by Pople and Gordon [46] to construct the geometrical models of 1, 2, 3, and 4, respectively.

All calculations are carried out on a CDC 6400 computer of the University of Ljubljana.

Results and Discussion

Total energies and the electronic populations of indole, isoindole, benzofuran, and isobenzofuran are given in Table 1 and Fig. 2, respectively.

Molecule	E_{tot} (a. u.)
Indole	−357.028678
Isoindole	−357.001836
Benzofuran	−376.544474
Isobenzofuran	−376.519020

Table 1. Total energies.

We shall not comment on the values of the total energies because the ab initio method is not very reliable in this respect [47].

However, the correct trends are obtained when the total energies of indole and benzofuran are compared with those of their isoconjugated isomers: isoindole and isobenzofuran, the former being large. Thus, the ab initio calculations prefer indole and benzofuran over isoindole and isobenzofuran, and

Table 2. Dipole moments (D).

Indole	Average exp. value [a]	:	2.08
	CNDO/2 value [48]	:	1.86
	VESCF value [49]	:	1.76
	Ab initio value	:	1.77
Isoindole	Ab initio value	:	2.20
Benzofuran	Experimental value [b]	:	0.79
	VESCF value [49]	:	0.52
	Ab initio value	:	0.64
Isobenzofuran	Ab initio value	:	0.38

[a] This value is a average of values taken from the following works: E. G. Cowley and J. R. Partington, J. Chem. Soc. **1936**, 47; E. G. Cowley, J. Chem. Soc. **1936**, 45; E. F. J. Janetzky and M. C. Lebret, Rec. Trav. Chim. **63**, 123 [1944].

[b] E. A. Schott-L'vova and Y. K. Syrkin, J. Phys. Chem. USSR **12**, 479 [1938].

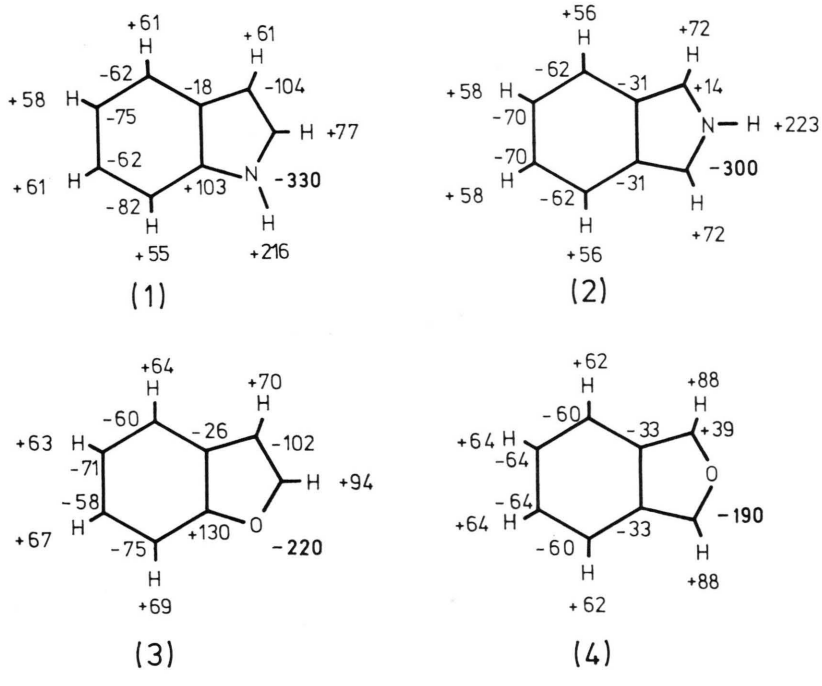


Fig. 2. Electron population for indole (1), isoindole (2), benzofuran (3), and isobenzofuran (4) (10^{-3} electron).

this is in agreement with earlier theoretical predictions [7, 16] and experimental findings [6]. Electronic densities have been used for the calculation of dipole moments. The calculated and available experimental dipole moments are given in Table 2. The CNDO/2 and VESCF values [48, 49] for indole and the VESCF value [49] for benzofuran are also included in Table 2. The agreement between the experimental and theoretical values is satisfactory.

The gross orbital charges in indole, isoindole, benzofuran, and isobenzofuran are summarized in Table 3. These results are interesting and worth

Table 3. Gross orbital charges.
(1) Indole

N	1 s = 1.9947	2 p σ = 2.1845	2 p = 3.9010	$\delta(\sigma) = -0.6115$	$s^{1.43}\,p^{2.18}$
	2 s = 1.4323	2 p π = 1.7165		$\delta(\pi) = 0.2835$	
	2 p_x = 1.0915			$\delta = -0.3280$	
	2 p_y = 1.7165				
	2 p_z = 1.0930				
C_2	1 s = 1.9929	2 p σ = 1.8222	2 p = 2.8564	$\delta(\sigma) = 0.0739$	$s^{1.11}\,p^{1.82}$
	2 s = 1.1110	2 p π = 1.0342		$\delta(\pi) = -0.0342$	
	2 p_x = 0.9540			$\delta = 0.0397$	
	2 p_y = 1.0342				
	2 p_z = 0.8682				
C_3	1s = 1.9927	2 p σ = 1.8903	2 p = 2.9876	$\delta(\sigma) = -0.0069$	$s^{1.12}\,p^{1.89}$
	2 s = 1.1239	2 p π = 1.0973		$\delta(\pi) = -0.0973$	
	2 p_x = 0.9271			$\delta = -0.1042$	
	2 p_y = 1.0973				
	2 p_z = 0.9632				
C_4	1 s = 1.9926	2 p σ = 1.8758	2 p = 2.9132	$\delta(\sigma) = 0.0194$	$s^{1.11}\,p^{1.88}$
	2 s = 1.1122	2 p π = 1.0374		$\delta(\pi) = -0.0374$	
	2 p_x = 0.945			$\delta = -0.0180$	
	2 p_y = 1.0374				
	2 p_z = 0.9308				
C_5	1 s = 1.9928	2 p σ = 1.9304	2 p = 2.9319	$\delta(\sigma) = -0.0609$	$s^{1.14}\,p^{1.93}$
	2 s = 1.1376	2 p π = 1.0015		$\delta(\pi) = -0.0015$	
	2 p_x = 0.9516			$\delta = -0.0624$	
	2 p_y = 1.0015				
	2 p_z = 0.9788				
C_6	1 s = 1.9927	2 p σ = 1.9176	2 p = 2.9448	$\delta(\sigma) = -0.0429$	$s^{1.13}\,p^{1.92}$
	2 s = 1.1326	2 p π = 1.0322		$\delta(\pi) = -0.0322$	
	2 p_x = 0.9660			$\delta = -0.0751$	
	2 p_y = 1.0322				
	2 p_z = 0.9516				
C_7	1 s = 1.9928	2 p σ = 1.9271	2 p = 2.9326	$\delta(\sigma) = -0.0565$	$s^{1.13}\,p^{1.93}$
	2 s = 1.1366	2 p π = 1.0055		$\delta(\pi) = -0.0055$	
	2 p_x = 0.9662			$\delta = -0.0620$	
	2 p_y = 1.0055				
	2 p_z = 0.9609				
C_8	1 s = 1.9927	2 p σ = 1.9072	2 p = 9630	$\delta(\sigma) = -0.0267$	$s^{1.13}\,p^{1.91}$
	2 s = 1.1268	2 p π = 1.0558		$\delta(\pi) = -0.0558$	
	2 p_x = 0.9378			$\delta = -0.0825$	
	2 p_y = 1.0558				
	2 p_z = 0.9694				
C_9	1 s = 1.9928	2 p σ = 1.7969	2 p = 2.8165	$\delta(\sigma) = 0.1223$	$s^{1.09}\,p^{1.80}$
	2 s = 1.0880	2 p π = 1.0196		$\delta(\pi) = -0.0196$	
	2 p_x = 0.8363			$\delta = 0.1027$	
	2 p_y = 1.0196				
	2 p_z = 0.9606				
H_{10}	1 s = 0.7837	$\delta(\sigma) = 0.2163$			
H_{11}	1 s = 0.9226	$\delta(\sigma) = 0.0774$			
H_{12}	1 s = 0.9394	$\delta(\sigma) = 0.0606$			
H_{13}	1 s = 0.9393	$\delta(\sigma) = 0.0607$			
H_{14}	1 s = 0.9421	$\delta(\sigma) = 0.0579$			
H_{15}	1 s = 0.9386	$\delta(\sigma) = 0.0614$			
H_{16}	1 s = 0.9447	$\delta(\sigma) = 0.0553$			

	(2) Isoindole				
N	1 s=1.9948 2 s=1.4473 2 p_x=1.1081 2 p_y=1.6305 2 p_z=1.1177	2 p σ=2.2258 2 p π=1.6305	2 p=3.8563	$\delta(\sigma)=-0.6679$ $\delta(\pi)=0.3695$ $\delta=-0.2984$	$s^{1.45}\,p^{2.23}$
C_2 (or C_9)	1 s=1.9928 2 s=1.0983 2 p_x=0.9098 2 p_y=1.1043 2 p_z=0.8804	2 p σ=1.7902 2 p π=1.1043	2 p=2.8945	$\delta(\sigma)=0.1187$ $\delta(\pi)=-0.1043$ $\delta=0.0144$	$s^{1.10}\,p^{1.79}$
C_3 (orC_8)	1 s=1.9926 2 s=1.1046 2 p_x=0.9357 2 p_y=1.0586 2 p_z=0.9395	2 p σ=1.8752 2 p π=1.0586	2 p=2.9338	$\delta(\sigma)=0.0276$ $\delta(\pi)=-0.0586$ $\delta=-0.0310$	$s^{1.10}\,p^{1.88}$
C_4 (or C_7)	1 s=1.9928 2 s=1.1352 2 p_x=0.9536 2 p_y=1.0040 2 p_z=0.9762	2 p σ=1.9298 2 p π=1.0040	2 p=2.9338	$\delta(\sigma)=-0.0578$ $\delta(\pi)=-0.0040$ $\delta=-0.0618$	$s^{1.14}\,p^{1.93}$
C_5 (or C_6)	1 s=1.9928 2 s=1.1336 2 p_x=0.9767 2 p_y=1.0177 2 p_z=0.9493	2 p σ=1.9260 2 p π=1.0177	2 p=2.9437	$\delta(\sigma)=-0.0524$ $\delta(\pi)=-0.0177$ $\delta=-0.0701$	$s^{1.13}\,p^{1.93}$
H_{10}	1 s=0.7761	$\delta(\sigma)=0.2239$			
H_{11} (or H_{16})	1 s=0.9284	$\delta(\sigma)=0.0716$			
H_{12} (or H_{15})	1 s=0.9437	$\delta(\sigma)=0.0563$			
H_{13} (or H_{14})	1 s=0.9421	$\delta(\sigma)=0.0579$			
	(3) Benzofuran				
O	1 s=1.9972 2 s=1.7787 2 p_x=1.1478 2 p_y=1.7346 2 p_z=1.5664	2 p σ=2.7142 2 p π=1.7346	2 p=4.4488	$\delta(\sigma)=-0.4901$ $\delta(\pi)=0.2654$ $\delta=-0.2247$	$s^{1.78}\,p^{2.71}$
C_2	1 s=1.9931 2 s=1.1151 2 p_x=0.9418 2 p_y=1.0572 2 p_z=0.8320	2 p σ=1.7738 2 p π=1.0572	2 p=2.8310	$\delta(\sigma)=0.1180$ $\delta(\pi)=-0.0572$ $\delta=0.0608$	$s^{1.12}\,p^{1.77}$
C_3	1 s=1.9928 2 s=1.1325 2 p_x=0.9348 2 p_y=1.0667 2 p_z=0.9752	2 p σ=1.9100 2 p π=1.0667	2 p=2.9767	$\delta(\sigma)=-0.0353$ $\delta(\pi)=-0.0667$ $\delta=-0.1020$	$s^{1.13}\,p^{1.91}$
C_4	1 s=1.9927 2 s=1.1154 2 p_x=0.9430 2 p_y=1.0375 2 p_z=0.9377	2 p σ=1.8807 2 p π=1.0375	2 p=2.9182	$\delta(\sigma)=0.0112$ $\delta(\pi)=-0.0375$ $\delta=-0.0263$	$s^{1.12}\,p^{1.88}$
C_5	1 s=1.9928 2 s=1.1375 2 p_x=0.9496 2 p_y=0.9993 2 p_z=0.9813	2 p σ=1.9309 2 p π=0.9993	2 p=2.9302	$\delta(\sigma)=-0.0612$ $\delta(\pi)=0.0007$ $\delta=-0.0605$	$s^{1.14}\,p^{1.93}$
C_6	1 s=1.9927 2 s=1.1336 2 p_x=0.9682 2 p_y=1.0233 2 p_z=0.9528	2 p σ=1.9210 2 p π=1.0233	2 p=2.9443	$\delta(\sigma)=-0.0473$ $\delta(\pi)=-0.0233$ $\delta=-0.0706$	$s^{1.13}\,p^{1.92}$

C_7	1 s=1.9928 2 s=1.1370 2 p_x=0.9677 2 p_y=1.0001 2 p_z=0.9605	2 p σ=1.9282 2 p π=1.0001	2 p=2.9283	$\delta(\sigma)=-0.0580$ $\delta(\pi)=-0.0001$ $\delta=-0.0581$	$s^{1.14}\ p^{1.93}$
C_8	1 s=1.9927 2 s=1.1275 2 p_x=0.9309 2 p_y=1.0453 2 p_z=0.9788	2 p σ=1.9097 2 p π=1.0453	2 p=2.9550	$\delta(\sigma)=-0.0299$ $\delta(\pi)=-0.0453$ $\delta=-0.0752$	$s^{1.13}\ p^{1.91}$
C_9	1 s=1.9929 2 s=1.0829 2 p_x=0.8042 2 p_y=1.0360 2 p_z=0.9539	2 p σ=1.7581 2 p π=1.0360	2 p=2.7941	$\delta(\sigma)=0.1661$ $\delta(\pi)=-0.0360$ $\delta=0.1301$	$s^{1.08}\ p^{1.76}$
H_{10}	1 s=0.9056	$\delta(\sigma)=0.0944$			
H_{11}	1 s=0.9304	$\delta(\sigma)=0.0696$			
H_{12}	1 s=0.9361	$\delta(\sigma)=0.0639$			
H_{13}	1 s=0.9374	$\delta(\sigma)=0.0626$			
H_{14}	1 s=0.9328	$\delta(\sigma)=0.0672$			
H_{15}	1 s=0.9314	$\delta(\sigma)=0.0686$			
	(4) Isobenzofuran				
O	1 s=1.9973 2 s=1.7958 2 p_x=1.6009 2 p_y=1.6728 2 p_z=1.1230	2 p σ=2.2739 2 p π=1.6728	2 p=4.3967	$\delta(\sigma)=-0.5170$ $\delta(\pi)=0.3272$ $\delta=-0.1898$	$s^{1.80}\ p^{2.72}$
C_2 (or C_9)	1 s=1.9930 2 s=1.1052 2 p_x=0.8893 2 p_y=1.1096 2 p_z=0.8639	2 p σ=1.7532 2 p π=1.1096	2 p=2.8628	$\delta(\sigma=0.1486$ $\delta(\pi)=-0.1096$ $\delta=0.0390$	$s^{1.11}\ p^{1.75}$
C_3 (or C_8)	1 s=1.9927 2 s=1.1106 2 p_x=0.9454 2 p_y=1.0434 2 p_z=0.9410	2 p σ=1.8864 2 p π=1.0434	2 p=2.9298	$\delta(\sigma)=0.0103$ $\delta(\pi)=-0.0434$ $\delta=-0.0331$	$s^{1.11}\ p^{1.89}$
C_4 (or C_7)	1 s=1.9928 2 s=1.1342 2 p_x=0.9489 2 p_y=1.0042 2 p_z=0.9798	2 p σ=1.9277 2 p π=1.0042	2 p=2.9319	$\delta(\sigma)=-0.0547$ $\delta(\pi)=-0.0042$ $\delta=-0.0589$	$s^{1.13}\ p^{1.93}$
C_5 (or C_6)	1 s=1.9928 2 s=1.1351 2 p_x=0.9804 2 p_y=1.0065 2 p_z=0.9498	2 p σ=1.9302 2 p π=1.0065	2 p=2.9367	$\delta(\sigma)=-0.0581$ $\delta(\pi)=-0.0065$ $\delta=-0.0646$	$s^{1.14}\ p^{1.93}$
H_{10} (or H_{15})	1 s=0.9121	$\delta(\sigma)=0.0879$			
H_{11} (or H_{15})	1 s=0.9382	$\delta(\sigma)=0.0618$			
H_{12} (or H_{13})	1 s=0.9362	$\delta(\sigma)=0.0638$			

commenting. The nitrogen and oxygen have the following charges:

N in indole:

$$(1\,s)^{1.99}\ (2\,s)^{1.43}\ (2\,p\,\sigma)^{2.18}\ (2\,p\,\pi)^{1.72},$$

N in isoindole:

$$(1\,s)^{1.99}\ (2\,s)^{1.45}\ (2\,p\,\sigma)^{2.23}(2\,p\,\pi)^{1.63},$$

O in benzofuran:

$$(1\,s)^{1.997}\ (2\,s)^{1.78}\ (2\,p\,\sigma)^{2.71}\ (2\,p\,\pi)^{1.73},$$

O in isobenzofuran:

$$(1\,s)^{1.997}\ (2\,s)^{1.80}\ (2\,p\,\sigma)^{2.72}\ (2\,p\,\pi)^{1.67}\,.$$

These values could be compared with the original (separated-atom) distribution:

nitrogen: $(1\,s)^2\ (2\,s)^2\ (2\,p\,\sigma)^1\ (2\,p\,\pi)^2$,

oxygen: $(1\,s)^2\ (2\,s)^2\ (2\,p\,\sigma)^2\ (2\,p\,\pi)^2$.

The above results show that nitrogen has gained 0.33 (in indole) and 0.30 (in isoindole) of an electron, respectively. Similarly, oxygen has gained 0.22 (in benzofuran) and 0.19 (in isobenzofuran) of an electron, respectively. This gain in both cases represents the sum of two effects: a gain from the σ orbitals and a loss from the π orbitals. Therefore, the charge transfer acts in two ways; both nitrogen and oxygen in all studied molecules are π donors and σ acceptors with the net result of a gain of charge. It is interesting to note that an ab initio study (using the contacted Gaussian set of 30 functions) by Clementi, Clementi, and Davies[50] gave the following charges on the nitrogen atom in pyrrole:

$$(1\,s)^2\ (2\,s)^{1.37}\ (2\,p\,\sigma)^{2.38}\ (2\,p\,\pi)^{1.66}\,.$$

The carbon atoms in 1, 2, 3, and 4 can be both σ and π acceptors or σ donors and π acceptors, depending on their positions within the bicyclic heteroconjugated molecule. Thus, the carbon atoms within the five-membered heterocyclic moiety are both σ and π acceptors whereas the four outer carbon atoms in the benzene ring are σ donors and π acceptors. The carbon atoms averagely have the following orbital charges:

$$(1\,s)^{1.99}\ (2\,s)^{1.12}\ (2\,p\,\sigma)^{1.88}\ (2\,p\,\pi)^{1.04}\,.$$

Finally, the hydrogen atoms are only σ donors.

Perhaps it is interesting to make a remark about the hybridization of nitrogen, oxygen, and carbon atoms in the title compounds. The hybridization of the nitrogen atom is

$$s^{1.43}\,p^{2.18}\ \text{(in indole)}$$

and

$$s^{1.45}\,p^{2.23}\ \text{(in isoindole)}.$$

Similarly, the hybridization of the oxygen atom is

$$s^{1.78}\,p^{2.71}\ \text{(in benzofuran)}$$

and

$$s^{1.80}\,p^{2.72}\ \text{(in isobenzofuran)}.$$

The hybridization on carbon atoms (averagely) in all studied molecules is

$$s^{1.12}\,p^{1.88}\,.$$

This value is not very different from the s^1 and p^2 of a trigonal hybrid on the carbon atom.

Table 4. π-electron charge densities.

Molecule	No. of atom	Momicchiolli and Rastelli[31]	Dewar et al.[7]	Klasinc et al.[36]	Present results
Indole	N	1.695	1.8766	1.6444	1.7165
	C_2	1.050	1.0191	1.0863	1.0342
	C_3	1.111	1.0427	1.0893	1.0973
	C_4	1.020	1.0278	1.0385	1.0374
	C_5	1.003	0.9873	0.9998	1.0015
	C_6	1.030	1.0176	1.0195	1.0322
	C_7	1.008	0.9912	1.0110	1.0055
	C_8	1.072	1.0300	1.0359	1.0558
	C_9	1.013	1.0077	1.0746	1.0196
Isoindole	N		1.8066	1.5380	1.6305
	$C_2(C_9)$		1.0589	1.1553	1.1043
	$C_3(C_8)$		1.0308	1.0468	1.0586
	$C_4(C_7)$		0.9983	1.0107	1.0040
	$C_5(C_6)$		1.0087	1.0182	1.0177
Benzofuran	O	1.874	1.9917	1.8246	1.7346
	C_2	1.040	0.9571	1.0320	1.0572
	C_3	1.033	1.0456	1.0532	1.0667
	C_4	0.983	1.0299	1.0235	1.0375
	C_5	1.008	0.9874	0.9995	0.9993
	C_6	1.010	1.0166	1.0115	1.0233
	C_7	1.002	0.9850	1.0040	1.0001
	C_8	1.035	1.0351	1.0254	1.0453
	C_9	1.014	0.9516	1.0264	1.0360
Isobenzofuran	O		1.9852	1.7585	1.6728
	$C_2(C_9)$		0.9660	1.0724	1.1096
	$C_3(C_8)$		1.0380	1.0333	1.0434
	$C_4(C_7)$		1.0005	1.0048	1.0042
	$C_5(C_6)$		1.0029	1.0102	1.0065

The results of Momicchiolli and Rastelli[31] and Klasinc et al.[36] agree with the ab initio values whereas those of Dewar et al.[7] differ considerably.

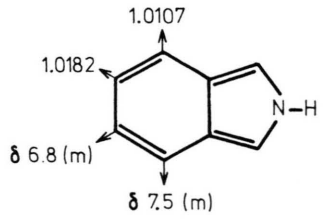
In Table 5 we give the correlation of experimental n.m.r. chemical shift data[51, 52] of indole and benzofuran with the total atom charge density of the adjacent aromatic carbon atoms calculated[53] by EHT and CNDO/2, and by us.

In both compounds the 3(β)-position has the greater charge density (in all three sets of calculations) and the smaller chemical shift. Note that the charge densities obtained from our calculations are

Table 5. Correlation of chemical shifts with total atom charge densities.

Compound	Carbon atom	Chemical shift δ (ppm)	Charge density EHT [53]	CNDO/2 [53]	Ab initio
Indole	2 (α)	6.68 [51]; 6.52 [52]	5.868	5.916	5.960
	3 (β)	6.38 ; 6.29	6.271	6.073	6.104
Benzofuran	2 (α)	7.56 [53]; 7.51 [52]	5.529	5.861	5.939
	3 (β)	6.68 ; 6.33	6.213	6.078	6.102

very similar to those obtained from the CNDO/2 calculations. This is not surprising because the CNDO/2 method [54] is parametrized in such a manner that the calculation should give the best fit between the CNDO and ab initio LCAO SCF charges in selected diatomic molecules. An interesting point concerns isoindole. It has been recently made [22] and its n.m.r. spectrum has been measured. The assignement of the multiplets centred at δ, 6.8 and 7.5, is made on the basis of the calculated π-electron densities in the benzenoid ring [36]:



This assignement is also supported by our calculations which have given the total charge densities 6.062 and 6.070 at the carbon atoms 4 and 5, respectively.

Finally, in Table 6 we report the first ionization potentials of indole, isoindole, benzofuran, and isobenzofuran estimated via Koopmans theorem. Ab initio calculations indicate that the first ionization potential is of the π-type, but the values are found to be rather low (approx. for 1.8 eV) when compared with experimental vertical ionization potentials. The same observation is made by other workers [55] when trying to predict the ionization potentials of large molecules using ab initio methods. However, our results reproduce the correct trends giving larger values of the first ionization potential to indole and benzofuran than to their less stable isoconjugated isomers. This is in accordance with the observation earlier made [56] that the differences in the ionization potentials run parallel to the differ-

Molecule	HOMO-LUMO separation (in a. u.)
Indole	0.4691
Isoindole	0.4269
Benzofuran	0.4756
Isobenzofuran	0.4127

Table 7. Ab initio HOMO-LUMO separation.

Table 6. First ionization potentials.

Molecule	First ionization potential (eV)									
	Calculated values								Experimental values [f, g]	
	ω-technique [a]	SCF π-MO approximate methods						Ab initio	Adiabatic	Vertical
		[b]	[c]	[d]	[e]	[f] adiabatic	[f] vertical			
Indole		8.21	8.33 8.44		8.32 8.98	8.36	8.70	6.0	7.75; 7.78	7.90
Isoindole						7.81	8.07	5.4		
Benzofuran	8.67		8.71 8.78	8.9	8.69 9.96	8.60	8.99	6.6	8.29; 8.42	8.36
Isobenzofuran						7.91	8.17	5.9		

[a] A. Streitwieser, Jr., J. Amer Chem. Soc. **82**, 4123 [1960].
[b] R. A. Sallavanti and D. D. Fitts, Internat. J. Quantum Chem. **3**, 33 [1969].
[c] Z. Yoshida and T. Kobayashi, Theor. Chim. Acta **20**, 216 [1970].
[d] H. A. Hammond, Theor. Chim. Acta **18**, 239 [1970].
[e] R. L. Flurry, Jr., E. W. Stout, and J. J. Bell, Theor. Chim. Acta **8**, 203 [1967].
[f] Ref. [7].
[g] J. H. D. Eland, J. Mass Spectrometry Ion Phys. **2**, 471 [1969].

ences in stability between the pairs of positional isomers. Therefore, the HOMO-LUMO separation should be also larger for more stable isomers. This is found (see Table 7) to be case.

[1] R. C. Elderfield, in "Heterocyclic Compounds", Edited by R. C. Elderfield, John Wiley, New York 1951, Vol. II, Chap. 2, p. 68.
[2] R. M. Acheson, An Introduction to the Chemistry of Heterocyclic Compounds, Interscience, New York 1960, p. 153.
[3] R. J. Sundberg, The Chemistry of Indoles, Academic Press, New York 1970.
[4] N. Trinajstić, Record Chem. Progress **32**, 85 [1971].
[5] L. Klasinc and N. Trinajstić, Tetrahedron **27**, 4045 [1971].
[6] R. Warrener, J. Amer. Chem. Soc. **93**, 2346 [1971].
[7] M. J. S. Dewar, A. J. Harget, N. Trinajstić, and S. D. Worley, Tetrahedron **26**, 4505 [1970].
[8] M. J. S. Dewar and T. Morita, J. Amer. Chem. Soc. **91**, 796 [1969].
[9] J. A. Pople, Trans. Faraday Soc. **49**, 1375 [1953].
[10] M. J. S. Dewar and G. J. Gleicher, J. Amer. Chem. Soc. **87**, 682 [1965].
[11] I. Gutman and N. Trinajstić, Chem. Phys. Letters **17**, 535 [1972].
[12] A. Baeyer, Liebigs Ann. **140**, 295 [1866].
[13] A. G. Perkin, J. Chem. Soc. **1870**, 368; ibid. **1871**, 295.
[14] L. Gatterman and A. E. Lockhart, Ber. Dtsch. Ges. **26**, 2808 [1893].
[15] DRE = Dewar's resonance energy; REPE = resonance energy per electron.
[16] B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., Tetrahedron **28**, 3657 [1972].
[17] L. F. Fieser and M. J. Haddadin, Can. J. Chem. **43**, 1599 [1965].
[18] R. Kreher and J. Seubert, Z. Naturforsch. **20 b**, 75 [1965].
[19] R. C. McCullogh, A. R. Rye, and D. Wege, Tetrahedron Letters **1969**, 5231.
[20] W. S. Wilson and R. N. Warrener, Tetrahedron Letters **1969**, 5231.
[20] W. S. Wilson and R. N. Warrener, Tetrahedron Letters **1970**, 5203.
[21] R. Bonnett and R. F. C. Brown, Chem. Comm. **1972**, 393.
[22] R. Bonnett, R. F. C. Brown, and R. G. Smith, J. C. S. Perkin **1**, 1432 [1973].
[23] M. Stoll. M. Winter, F. Gautschi, I. Flament, and B. Willhalm, Helv. Chim. Acta **50**, 628 [1967].
[24] A. J. Aasen, B. Kimland, S.-O. Alquist, and C. R. Enzell, Acta Chem. Scand. **25**, 1382 [1971].
[25] G. Neurath, J. Gewe, and H. Wichern, Beitr. Tabakforsch. **4**, 250 [1968].
[26] K. Kaiser, Z. Krebsforsch. **59**, 488 [1953].
[27] R. Royer, E. Bisagni, M. Hubert-Habart, L. Rene, and J.-P. Marquet, Bull. Chem. Soc. France **1965**, 1794.
[28] M. J. S. Dewar, Trans. Faraday Soc. **42**, 764 [1946].
[29] H. C. Longuet-Higgins and C. A. Coulson, Trans. Faraday Soc. **43**, 87 [1947].
[30] J. Kopecky, J. E. Shields, and J. Bornstein, Tetrahedron Letters **1967**, 3669.
[31] F. Momicchiolli and J. Rastelli, J. Mol. Spectroscopy **22**, 310 [1967].
[32] F. P. Billingsley, II, and J. E. Bloor, Theor. Chim. Acta Berlin **11**, 325 [1968].
[33] J. Fabian, A. Mehlhorn, and R. Zahradnik, Theor. Chim. Acta Berlin **12**, 247 [1968].
[34] R. B. Herman, Internat. J. Quantum Chem. **2**, 165 [1968].
[35] M. J. S. Dewar and N. Trinajstić, J. Chem. Soc. A **1971**, 1220.
[36] L. Klasinc, E. Pop, N. Trinajstić, and J. V. Knop, Tetrahedron **28**, 3465 [1972].
[37] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 [1951].
[38] J. M. Foster and S. F. Boys, Rev. Mod. Phys. **32**, 303 [1960].
[39] C. M. Reeves and R. Fletcher, J. Chem. Phys. **42**, 4073 [1965].
[40] K. O-ohata, H. Taketa, and S. Huzinaga, J. Phys. Soc. Japan **21**, 2306 [1966].
[41] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 [1969].
[42] W. J. Hehre and J. A. Pople, J. Amer. Chem. Soc. **92**, 2191 [1970].
[43] R. S. Mulliken, J. Chem. Phys. **23**, 1833, 1841, 2338, 2343 [1955].
[44] A. W. Hanson, Acta Cryst. **17**, 559 [1964].
[45] P. T. Clarke and J. M. Spink, Acta Cryst. B **25**, 162 [1969].
[46] J. A. Pople and M. Gordon, J. Amer. Chem. Soc. **89**, 4253 [1967].
[47] M. J. S. Dewar, Topics Cur.. Chem. **23**, 1 [1971].
[48] J. E. Bloor and D. L. Breen, J. Amer. Chem. Soc. **89**, 6835 [1967].
[49] R. D. Brown and B. A. W. Collier, Theoret. Chim. Acta Berlin **7**, 259 [1967].
[50] E. Clementi, H. Clementi, and D. R. Davies, J. Chem. Phys. **46**, 4725 [1967].
[51] J. A. Elvidge and R. G. Foster, J. Chem. Soc. **1963**, 590: ibid. **1964**, 981.
[52] L. A. Cohen, J. W, Daly, H. Kny, and R. Witkop, J. Amer. Chem. Soc. **82**, 2184 [1960].
[53] R. B. Herman, Internat. J. Quantum Chem. **2**, 165 [1968].
[54] J. A. Pople and G. A. Segal, J. Chem. Phys. **44**, 3289 [1966].
[55] e. g.: R. E. Christoffersen, J. Amer. Chem. Soc. **93**, 4104 [1972].
[56] M. J. S. Dewar and N. Trinajstić, Croat. Chem. Acta **42**, 1 [1970]; Tetrahedron **26**, 4269 [1970].