version was practically complete (no bands of the parent compound were seen in the spectra after metalation). Organic anions are not soluble in common spectroscopic solvents and react with some of them, so the use of aprotic solvents (usually DMSO or DMSO-d_6 [20, 29]) is necessary in these cases.

The IR spectra were recorded on a Bruker IFS 113v FTIR spectrometer in a CaF$_2$ cell of 0.13 mm path length, at a resolution of 1 cm^{-1} and 50 scans.

COMPUTATIONS

The quantum chemical calculations were performed using the GAUSSIAN-98 program package [30]. We employed B3LYP (Becke's three-parameter method [31] using the correlation functional of Lee, Yang and Parr [32] and standard 6-31++G** basis set. The stationary points found on the molecular potential energy hypersurfaces were characterized using standard harmonic vibrational analyses. Use of the above basis set in the computations has recently given better or equally good structural predictions, compared to other basis sets for both molecules and/or anions [27, 29, 33] (and references therein). No scaling in the density functional force field was done. To estimate the effect of a polar medium (DMSO) on the fundamental vibrational frequencies and intensities of the species studied we applied the Onsager SCRF method [34, 35] and DFT at the same level of theory (B3LYP/6-31++G**). In order to improve the visual representation of the calculated spectra in the figures, the calculated absorption lines were replaced by Lorentz functions with a half-width of 10 cm^{-1} by the SimOpus program [36] (see Fig. 2).

RESULTS AND DISCUSSION

Energy analysis

Optimized total energies (E^{tot}), Gibbs free energies (G) and vibrational zero-point energies (ZPVE) calculated for the species studied in the gas state and DMSO solution are given in Table 1.

The deprotonation energy (E^D) of isatin was calculated as a difference between the corrected total energies ($E^{tot}_{corr.}$) of the azanion and molecule:

$$\Delta E^{tot}_{corr.} = E^{tot}_{corr.} \text{ (anion)} - E^{tot}_{corr.} \text{ (molecule)}$$

(Table 1).

The E^D values are related to the gas-phase acidities of Broensted acids and could also be used as an approximate measure of their pKa values in polar aprotic solvents [37]. There is a fair linear correlation between gas-phase pKa and DMSO pKa values for 97 H-C acids of various structures [38]. We have recently found a linear correlation between B3LYP/6-31++G** $\Delta E^{tot}_{corr.}$ and pKa (solvent DMSO) for a series of C–H, N–H and O–H acids containing cyano and/or carbonyl groups [33]:

$$pKa(DMSO) = 0.1150 \Delta E^{tot}_{corr.} \text{ [kJ·mol}^{-1}] - 150.04.$$

This equation has successfully been used to estimate pKa of moderate [39] and superstrong [40] organic acids. We did not find in the literature any pKa (DMSO) data for isatin. The calculated E^D value is not away from those of p-hydroxyacetophenone (1383.6 kJ·mol^{-1} [25] and of p-hydroxybenzonitrile (1402.11 kJ·mol^{-1} [21], so the title compound should be a moderately weak Broensted N–H acid. In fact, pKa of p-hydroxyacetophenone is 11.9 (DMSO) [41] and 8.05 (O–H)[41]; the corresponding values of p-hydroxybenzonitrile are 13.1 and 7.97, respectively [42, 43]. Having in mind the above equation and the B3LYP/6-31++G** $\Delta E^{tot}_{corr.}$ of 1400.1 kJ·mol^{-1} (Table 1 the last line), we calculated pKa (DMSO) of isatin near 11.07.

Correlation analysis

We obtained the following linear correlation between theoretical and experimental IR frequencies of isatin: $\nu_{exp} = 0.9343 \nu_{theor} + 64.45$ (cm^{-1}), correlation coefficient R = 0.9998; standard deviation s.d. = 13.5; number of data points n = 15. According to Jaffe's classification [44], the correlation is excellent, with 1 > R > 0.99. We shall use it for correlational scaling of the theoretical frequencies in the next section.

Table 1. Total energies (E), Gibbs free energies (G), zero-point vibrational energies (ZPVE) of isatin and its azanion.

Species	Gas-phase			DMSO solution		
	E, a.u.	G, a.u.	ZPVE, kJ·mol^{-1}	E, a.u.	G, a.u.	ZPVE, kJ·mol^{-1}
Molecule	513.095037	513.012950	302.29	513.102387	513.020158	302.51
Azanion	512.547945	512.479470	266.01	512.560381	512.491463	266.96
$\Delta E^{tot}_{corr.} = E^{tot}_{corr.}$ (azanion) $- E^{tot}_{corr.}$ (molecule)	1400.11			1387.48		

Spectral analysis

Tables 2 and 3 contain theoretical and experimental IR data for isatin and its azanion, respectively. We can find there a good agreement between experimental and scaled theoretical frequencies. The mean absolute deviations between them are 9.6 cm⁻¹ for isatine and 10.5 cm⁻¹ for its azanion. These values are within the corresponding mean deviation intervals of 9±20 and 9±24 cm⁻¹, typical for DFT calculations for series of molecules and anions, containing cyano and/or carbonyl groups [23-29] (and references therein).

We can state the following further comments on the results in Table 2:

‹ ν_{N-H} at 3444 cm⁻¹ (solvent carbon tetrachloride) corresponds to hydrogen-bond free N-H groups.

The ν_{N-H} band (solvent DMSO) is broad and complex, due to the formation of strong N-H....O=S hydrogen bonds between isatine and solvent. The carbonyl stretchings $\nu_{C=O}$ at 1740 cm⁻¹ with shoulder at 1757 cm⁻¹ correspond to C=O and C=O groups. According to the calculations there is a vibrational interaction between the two carbonyl groups. The higher-frequency mode can be described as asymmetrical stretch of the (C=O)(C=O) fragment, where the (α-C=O) coordinate is predominant. The lower-frequency mode corresponds to the symmetrical stretch of the same fragment; in this case (β-C=O) coordinate is predominant.

‹ The δ_{N-H} coordinate is strongly delocalized, taking part in vibrations Nos. 12-15 of isatin (Table 2).

Table 2. Theoretical (SCRF model) and experimental (DMSO) data for isatin.

No.	B3LYP/6-31++G**			Approximate Description [a]	Experimental data [b]	
	N, cm⁻¹	N, cm⁻¹ [c]	A, km·mol⁻¹		N, cm⁻¹	A, km·mol⁻¹
1.	3638	3464	81.0	ν_{NH}	3444 [d]	
2.	3223	3075	3.9	ν_{PhH}		
3.	3213	3066	6.3	ν_{PhH}	3074	5.1
4.	3205	3059	0.3	ν_{PhH}		
5.	3200	3054	2.2	ν_{PhH}		
6.	1811	1757	387.1	$\nu_{ul(C1O)}$, $\nu_{vl(C1O)}$	1757	68.8
7.	1789	1736	877.9	$\nu_{vl(C1O)}$, $\nu_{ul(C1O)}$	1740	216.8
8.	1657	1612	693.6	ν_{Ph}, PhH, δ_{PhNC}	1621	110.2
9.	1639	1596	94.3	b_{Ph}, δ_{PhH}	1611	12.1
10.	1517	1482	40.4	δ_{PhH}, ν_{Ph}	1487	3.1
11.	1500	1466	147.8	δ_{PhH}, ν_{Ph}	1470	43.5
12.	1408	1380	73.6	δ_{NH}, δ_{PhH}, δ_{CNC}	1398	2.2
13.	1359	1334	110.0	b_{Ph}, δ_{NH}, δ_{PhH}, δ_{PhNC}	1328	28.2
14.	1310	1289	76.2	b_{Ph}, δ_{NH}, δ_{PhH}, δ_{PhNC}	1289	12.1
15.	1265	1246	19.0	δ_{NH}, δ_{PhH}, δ_{PhNC}	1218	8.3
16.	1215	1200	25.1	δ_{PhH}, ν_{Ph}, δ_{PhCC}	1199	11.9
17.	1205	1190	106.4	δ_{NCC}, δ_{PhH}, δ_{Ph}	1189	10.5
18.[f]	1175	1162	51.8	δ_{Ph}, δ_{PhH}, δ_{NCC}	1147	2.8

[a] Vibrational modes: ν, stretching; δ, in-plane bendings; [b] Measured after having decomposed the complex bands into components; [c] Scaled according to the correlation equation $N_{scal} = 0.9345 \, N_{theor} + 64.45$ (cm⁻¹), correlation coefficient R = 0.9998, standard deviation s.d. = 13.5; number of data points n = 15; [d] in carbon tetrachloride; [f] Followed by 24 lower-frequency normal vibrations.

Table 3. Theoretical (SCRF model) and experimental (DMSO-d$_6$) data for isatin azanion.

No.	B3LYP/6-31++G**			Approximate	Experimental data	
	N, cm^{-1}	N, cm^{-1} [c]	A, km·mol^{-1}	Description [a]	N, cm^{-1}	N, cm^{-1} [c]
1.	3206	3060	30.4	ν_{PhH}	3057	2.3
2.	3190	3045	53.5	ν_{PhH}	3050	5.1
3.	3175	3031	8.0	ν_{PhH}	3045	2.3
4.	3171	3027	26.0	ν_{PhH}	3042	2.5
5.	1748	1698	578.6	$\nu_{\nu!\,(C1O)}$	1716	119.3
6.	1682	1636	206.1	$\nu_{\nu!\,(C1O)}$, ν_{Ph}, δ_{PhNC}, δ_{PhH}	1648	74.3
7.	1621	1579	1186.7	ν_{Ph}, δ_{PhH}, δ_{CCC}, $\nu_{\nu!\,(C1O)}$	1600	248.6
8.	1593	1553	1011.6	ν_{Ph}, δ_{PhH}, δ_{CCN}	1568	134.7
9.	1503	1468	200.8	δ_{Ph}, δ_{PhH}	1470	61.7
10.	1463	1431	356.9	δ_{PhH}, δ_{Ph}	1439	92.7
11.	1341	1318	140.3	δ_{PhH}, δ_{Ph}	1320	42.5
12.	1330	1307	407.4	δ_{PhH}, δ_{PhNC}	1291	31.1
13.	1262	1244	112.4	δ_{PhNC}, δ_{PhH}, δ_{Ph}	1243	16.5
14.	1244	1227	225.3	δ_{PhNC}, δ_{PhH}, δ_{Ph}	1224	18.7
15.	1199	1185	3.1	δ_{PhH}, δ_{PhCC}, δ_{Ph}	1210	13.8
16.[d]	1153	1142	181.8	δ_{PhH}, δ_{Ph}, ν_{NCC}	1133	32.5

[a-c] See footnotes to Table 2. [d] Followed by 23 lower-frequency normal vibrations.

The conversion of isatin into azanion is accompanied by the following essential changes in the IR spectrum (cf. Tables 2, 3 and Figs. 1, 2):
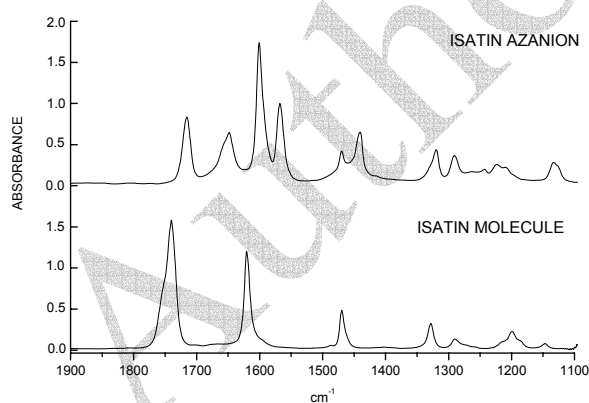

Fig. 1. IR spectra of isatin and isatin azanion in DMSO-d$_6$ (0.09 mol·l^{-1})

‹ The absence of a N H group in the azanion cancels the N H vibration and the influence of the δ_{N-H} coordinate on the low-frequency vibrations (cf. above).

‹ Due to the strong direct resonance between the α-carbonyl group and azanionic center the $\nu_{C=O}$ frequency undergoes an essential lowering: calculated 121 cm^{-1}, measured 109 cm^{-1}. The computations predict participation of $\nu_{C=O}$ coordinate also in vibration No. 7.

‹ Again due to the resonance, indirect in this case, the β-carbonyl stretching frequency undergoes a lowering, but not so strong: calculated 39 cm^{-1}, measured 24 cm^{-1}.

‹ In agreement between theory and experiment, the conversion of the molecule into azanion causes 2-fold increase in the integrated intensity of the 8a-type phenylene ring band.
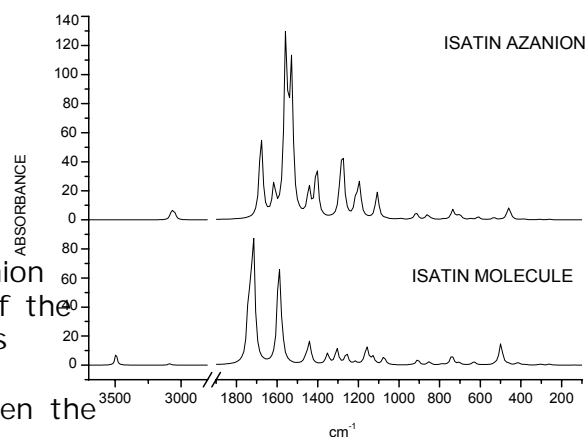

Fig. 2. Theoretical (B3LYP 6-31++G**, SCRF) IR spectra of isatin and isatin azanion.

436

Structural analysis

Theoretical and experimental steric structural parameters of the species studied are compared in Table 4. The comparison of calculated with X-ray values for the molecule shows a good agreement between them. The mean absolute deviations are:

$$\text{m.a.d.} = \frac{1}{n}\sum |R_i^{theor} - R_i^{exp}| \text{ of } 0.0408\,\text{Å and}$$

$$\text{m.a.d.} = \frac{1}{n}\sum |A_i^{theor} - A_i^{exp}| \text{ of } 0.71°.$$

ture. Having in mind the low m.a.d values for the molecule we assume that the structural parameters calculated by the same method for its azanion should also be adequate. So, we could estimate the steric structure charge, caused by the conversion of isatine into azanion:
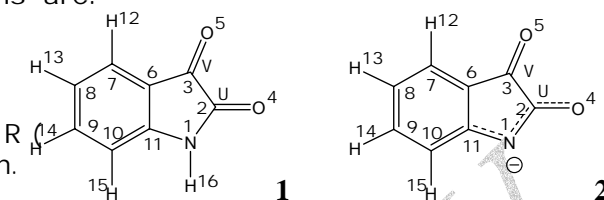
Scheme 1. Atom numbering of the isatin **1** and its azanion **2**.

Table 4. Theoretical and experimental bond lengths R (Å) and angles A (°) in the isatin molecule and its azanion.

| | B3LYP/6-31++G** | | | X-ray |
	molecule	azanion	Δtheor(ion-mol)	molecule
R(1,2)[b]	1.3848	1.3594	**−0.0254**	1.3553
R(1,11)	1.4043	1.374	**−0.0303**	1.4073
R(1,16)	1.0104	-	-	0.943
R(2,3)	1.2110	1.2349	**0.0239**	1.2203
R(2,4)	1.5747	1.5958	**0.0211**	1.5623
R(4,5)	1.2119	1.2238	**0.0119**	1.2113
R(4,6)	1.4717	1.4643	0.0074	1.4593
R(6,7)	1.3936	1.3906	0.0030	1.3883
R(6,11)	1.4100	1.4315	**0.0215**	1.4013
R(7,8)	1.3981	1.4008	0.0027	1.3824
R(7,12)	1.0857	1.0887	0.0030	0.973
R(8,9)	1.4019	1.4105	0.0086	1.4044
R(8,13)	1.0849	1.0868	0.0019	0.983
R(9,10)	1.4027	1.3952	0.0075	1.3900
R(9,14)	1.0861	1.0893	0.0032	0.963
R(10,11)	1.3898	1.4139	**0.0241**	1.3743
R(10,15)	1.0856	1.0868	0.0012	0.923
m.a.d.[c]	0.0408			
A(2,1,11)	112.13	106.9567	**−5.1767**	111.42
A(2,1,16)	122.73	-	-	121.2
A(11,1,16)	125.13	-	-	127.2
A(1,2,3)	127.14	128.7038	1.5569	127.62
A(1,2,4)	104.86	109.2387	**4.3752**	105.82
A(3,2,4)	127.98	122.0575	**−5.9321**	126.62
A(2,4,5)	124.43	126.8649	2.4338	123.92
A(2,4,6)	104.89	103.0657	1.8338	104.90
A(5,4,6)	130.66	130.0694	0.5999	131.42
A(4,6,7)	131.37	132.5628	1.1849	132.42
A(4,6,11)	107.78	104.7719	3.0107	107.22
A(7,6,11)	120.83	122.6653	1.8258	120.43
A(6,7,8)	118.61	119.0714	0.4531	118.72
A(6,7,12)	119.85	119.7708	0.0866	120.02
A(8,7,12)	121.52	121.1577	0.3666	121.2
A(7,8,9)	119.98	118.9368	1.0496	119.91
A(7,8,13)	120.20	120.8127	0.6059	121.2
A(9,8,13)	119.80	120.2505	0.4437	119.2
A(8,9,10)	121.94	122.4936	0.5511	122.02
A(8,9,14)	119.29	118.7754	0.5210	119.2
A(10,9,14)	118.76	118.7309	0.0302	119.2
A(9,10,11)	117.48	119.2392	1.7571	117.2
A(9,10,15)	120.90	121.1289	0.2287	119.2
A(11,10,15)	121.61	119.6318	1.9859	123.2
A(1,11,6)	110.32	115.9669	**5.6460**	110.7
A(1,11,10)	128.54	126.4395	2.1083	127.5
m.a.d.[c]	0.71			

[a] Ref. 16. [b] For atom numbering see Scheme 1. [c] Mean absolute deviation between theoretical and experimental values.

There are not in the literature any experimental (X-ray or other) data for the isatine azanion struc-

Like in many other cases [27 29] (and reference therein), the **1**→**2** conversion causes strong bond length changes at and next to the anionic center (Table 4 Δ values in bold). They are strong shortenings of the N^1C^{11} and N^1C^2 bonds and strong lengthenings of the C^2C^3 and C^6C^{11} bonds.

Bond lengthenings take place of C^2C^4 and C^4O^5 bonds. The C^2C^4 bond in isatin (Table 4) is one of the longest dicarbonyl bond reported [15, 16] and probably responsible for cleavage of the five-membered ring in alkali media.

The strongest bond angle changes caused by the **1**→**2** conversion correspond to the 5-membered ring.

The natural bond orbital (NBO) net electric charges q_i on atoms of the species studied are listed in Table 5. The net charges distribution over fragments of the species studied are as follows: 0.003, 0.075, 0.125 and 0.197, for β-carbonyl group, α-carbonyl group, phenylene ring and amido group, respectively, of the isatin molecule, and 0.086, 0.083, 0.165 and 0.665, for β-carbonyl group, α-carbonyl group, phenylene ring and azanionic centre, respectively, of the isatine azanion.

Table 5. Calculated NBO atomic charges (q) for isatin and its azanion (For atom numbering see Scheme 1).

Atom[a]	q(molecule)	q(azanion)
N^1	0.645	0.665
C^2	0.613	0.556
O^3	0.538	0.639
C^4	0.482	0.483
O^5	0.484	0.569
C^6	0.202	0.245
C^7	0.151	0.180
C^8	0.265	0.335
C^9	0.178	0.213
C^{10}	0.277	0.296
C^{11}	0.199	0.209
H^{12}	0.259	0.230
H^{13}	0.247	0.217
H^{14}	0.246	0.216
H^{15}	0.248	0.231
H^{16}	0.447	
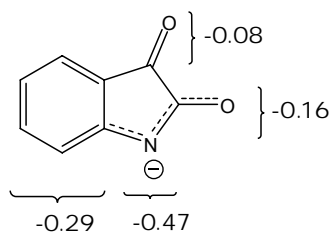
Scheme 2. The natural bond orbital (NBO) azanionic changes distribution over fragments of the isatin azanion.

The differences $\Delta q_i = q_i(anion) - q_i(molecule)$ are quite informative to show the distributions of the new (carbanionic, azanionic, etc.) electric charges in anions [23–29] (and references therein). We can see in Scheme 2, that according to the computations 0.08 e, 0.16 e and 0.29 e of the new azanionic charge are delocalized over the β-carbonyl group, α-carbonyl group and phenylene ring, respectively, and 0.47 e of it is remain localized at the azanionic center.

CONCLUSION

We found in this study a good agreement between theoretical and experimental IR data for both the isatin molecule 1 and its azanion 2. Use of the same theoretical method and basis set made it possible to describe well both the steric and electronic structure of the molecule 1. On the basis of these results we assumed that the structural pre-dictions for the azanion 2 should also be adequate.

REFERENCES

1. O. Erdmann, J. Prakt. Chem., 24, 1 (1841).
2. T. Sandmayer, Helv. Chim. Acta, 2, 234 (1919).
3. V. Glover, J. M. Halket, P. J. Watkins, A. Clone, B. L. Goodwin, M. Sandler, J. Neurochem., 51, 656 (1988).
4. S. K. Bhattacharya, V. Glover, I. McIntyre, G. Oxenkrug, M. Sandler, Neurosci. Lett., 92, 218 (1982).
5. S. K. Bhattacharya, S. Mitra, S. B. Acharya, J. Psychopharmacol., 5, 202 (1991).
6. A. Cane, M. C. Tournaire, D. Barritault, M. Crumeyrolle-Arias, Biochem. Biophys. Res. Commun., 276, 379 (2000).
7. The Merck Index, 13 Edn., Merck & Co. Inc., Whitehouse Station, N.J., USA, 2001.
8. A. A. Jarrahpour, D. Khalili, Molbank, M437 (2005).
9. S. N. Pandeya, D. Sriram, G. Nath, E. De Clercq, Arzneimittel Forschun./Drug Res., 50, 55 (2000).
10. S. K. Sridhar, S. N. Pandeya, J. P. Stables, S. K. Armes, Eur. J. Pharm. Sci., 16, 129 (2002).
11. A. M. A. Hassaan, Transit. Met. Chem., 15, 283 (1990).
12. A. Garcia-Raso, J. J. Fiol, G. Molins, A. M. Calafat, P. A. Marzilli, L. G. Marzilli, Metal-Based Drugs, 2, 81 (1995).
13. P. Naumov, F. Atanasov, Bull. Chem. Thechnol. Macedonia, 19, 1 (2000).
14. G. H. Goldschmidt, F. J. Llewellyn, Acta Cristallogr., 3, 294 (1950).
15. M. H. Palmer, A. J. Blake, R. O. Gould, Chem. Phys., 115, 219 (1987).
16. M. A. Frolova, V. N. Kravtsov, V. N. Biyushkin, Y. M. Chumakov, O. N. Belkov, T. I. Malynovskii, Zh. Strukt. Khim., 29, 155 (1988).
17. A. Bigatto, V. Galasso, Spectrochim. Acta, 35 A, 725 (1979).
18. B. N. Narziev, N. Mulloev, J. Struct. Chem., 40, 481 (1999).
19. P. Naumov, F. Atanasov, Spectrochim. Acta, 57 A, 469 (2001).
20. N. Juchnovski, I. G. Binev, in: The Chemistry of Functional Groups, Suppl. C, S. Patai, Z. Rappoport (Eds), Wiley, New York, 1983, Ch. 4.
21. V. Ognyanova, J. Petrov, G. N. Andreev, Spectrosc. Lett., 30, 933 (1997).
22. G. N. Andreev, O. K. Argirov, V. Ognyanova, J. Mol. Struct., 516, 238 (2000).
23. I. G. Binev, P. J. Vassileva-Boyadjieva, Y. I. Binev, J. Mol. Struct., 447, 235 (1998).
24. Ye. I. Binev, Ch. T. Petkov, L. Pejov, Spectrochim. Acta Part A, 56, 1949 (2000).
25. P. J. Vassileva-Boyadjieva, E. A. Velcheva, Y. I. Binev, Bulg. Chem. Commun., 37, 313 (2005).
26. M. K. Georgieva, P. N. Angelova, I. G. Binev, J. Mol. Struct., 692, 23 (2004).
27. D. Popova, M. K. Georgieva, O. I. Petrov, K. V. Petrova, E. A. Velcheva, Int. J. Quant. Chem., 107, 1752 (2007).
28. L. I. Daskalova, E. A. Velcheva, I. G. Binev, J. Mol. Struct., 826, 198 (2007).
29. E. A. Velcheva, B. A. Stamboliyska, J. Mol. Struct., (2007) in press.
30. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayak-kara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.
31. A. D. Becke, Phys. Rev. A, 38, 3098 (1988).
32. C. Lee, W. Yang, R. G. Parr, Phys. Rev. B, 37, 785 (1988).

33. M. K. Georgieva, E. A. Velcheva, *Int. J. Quant. Chem.*, **106,** 1316 (2006).

34. M. W. Wong, M. J. Frisch, K. B. Wiberg, *J. Am. Chem. Soc.*, **113**, 4776 (1990).

35. O. Tapia, O. Goscinski, *Mol. Phys.*, **29**, 1653 (1975).

36. Y. I. Binev, Ph.D. Thesis, Inst. Org. Chem., Bulgarian Academy of Sciences, Sofia, 2000.

37. V. M. Vlasov, L. A. Oshkina, *Org. React.*, **28**, 47 (1993).

38. I. A. Koppel, J. Koppel, V. Pihl, I. Leito, M. Mishima, V. M. Vlassov, L. M. Yagupolski, R. W. Taft, *J. Chem. Soc. Perkin Trans.*, 1125 (2000)

39. L. I. Daskalova, *J. Mol. Struct.*, in press.

40. J. A. Tsenov, S. S. Stoyanov, I. G. Binev, *Bulg. Chem. Commun.*, **37**, 361 (2005).

41. A. P. Kreshkov, N. Sh. Aldarova, A. I. Tarassov, V. A. Vasnyev, S. V. Vinogradova, M. V. Slavgorodska, T. I. Mitaishvili, V. V. Korshak, *Org. Reactivity*, **7**, 279 (1970).

42. J. K. Ellington, E. M. Arnet, *J. Am. Chem. Soc.*, **110**, 7778 (1988).

43. A. Fini, P. De Maria, A. Guarnjeri, L. Varoli, *J. Pharm. Sci.*, **76**, 48 (1987)

44. H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

ЕКСПЕРИМЕНТАЛНО И ТФП ИЗСЛЕДВАНЕ НА ИЧ СПЕКТРАЛНИ И СТРУКТУРНИ ПРОМЕНИ ПРОИЗТИЧАЩИ ОТ ПРЕВРЪЩАНЕТО НА 1Н-ИНДОЛ-2,3-ДИОН (ИЗАТИН) В АЗАНИОН

Ев. А. Велчева*, П. Ж. Василева-Бояджиева, Ив. Г. Бинев

Лаборатория „ Структурен органичен анализ", Институт по органична химия с център по фитохимия, Българска академия на науките, ул. „Акад. Г. Бончев", бл. 9, 1113 София

(Резюме)

ИЧ спектрални и структурни промени, произтичащи от превръщането на 1Н-индол-2,3-дион (изатин) в азанион са изследвани чрез спектроскопски експерименти и B3LYP/6-31++G** пресмятания в рамките на модела на Онзагер. Намерено е добро съответствие между експериментални и скалирани ИЧ честоти. В съгласие между теория и експеримент, превръщането предизвиква 109 cm^{-1} понижение на α-карбонилната валентна честота, 24 cm^{-1} понижение на β-карбонилната валентна честота и други съществени спектрални промени. Същия теоретичен метод дава добро описание на пространствената и електронна структура на изатина. Според изчисленията, 0.76 e (NBO) от новия (азанионен) заряд на аниона е делокализиран в ароматния остатък и азанионния център.