

Experimental and DFT studies on IR spectral and structural changes arising from the conversion of 1H-indole-2,3-dione (isatin) into azanion

E. A. Velcheva*, P. J. Vassileva-Boyadjieva, I. G. Binev

Department of Structural Organic Analysis, Institute of Organic Chemistry with Centre of Phytochemistry,
Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 9, 1113 Sofia, Bulgaria

Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

Received December 17, 2007; Revised January 25, 2008

IR spectral and structural changes, arising from the conversion of 1H-indole-2,3-dione (isatin) into azanion have been studied by IR spectra and quantum chemical calculation within the Onsager self-consistent reaction field (SCRf), using a density functional theory (DFT) method at the B3LYP/6-31++G** level. A good agreement has been found between experimental and scaled theoretical IR frequencies. In agreement between theory and experiment, the conversion causes a 109 cm⁻¹ decrease in the α -carbonyl stretching frequency, 24 cm⁻¹ decrease in the β -carbonyl stretching frequency and other essential IR spectral variations. The same theoretical method has given good descriptions both of steric and electronic structures of isatin. According to the computations, the changes in natural bond orbital (NBO) charges indicate that the 0.76e⁻ of the new (azanionic) charge of the azanion are delocalized within the aromatic residue and azanionic center.

Key words: IR, DFT B3LYP, structure, 1H-indole-2,3-dione, (isatin), azanion.

INTRODUCTION

1H-Indole-2,3-dione (isatin) was discovered in the nineteenth century as an oxidation product of pigment indigo [1] and first prepared synthetically by Sandmayer in 1919 [2]. Isatin was found in mammalian body fluids and tissues, isolated as an endogenous compound in 1988 [3] and reported to possess a wide range of central nervous system activities [4, 5], as well as to inhibit the neuroblastoma cell line proliferation at submicromolar concentrations; the potential utility of isatin as antitumor agent was also discussed [6]. Isatin class compounds are used mainly as precursors in dyes manufacturing (including hair dye) and in analytical chemistry [7]. The synthetic versatility of isatin has led to the extensive use of this compound in synthesis of pharmaceuticals, herbicides, *etc.* Schiff bases of isatin were reported to possess interesting pharmaceutical properties [8], such as anti-HIV [9] and anticonvulsant [10] ones. Isatin and its derivatives have also been used as ligands for complexation with various metal ions and the biological activities of these complexes were investigated [11–13]. It was found, that the structural properties of substituted isatins could be related with their biological activity.

The crystal structure of isatin was determined in 1950 [14], but because of the low accuracy of the

data, it was redetermined later [15, 16]. Contrary to the parent molecule, there are no structural data on its azanion.

The vibrational spectra of isatin have previously been studied [17–19]. The assignment of most of the observed frequencies has been assumed on the basis of IR and Raman spectra and dichroism of the single crystal [17]. The proton-donor ability of isatine when its H-form participated in complexes with organic bases were investigated by IR spectroscopy [18]. *Ab initio* theoretical as well as experimental data on the FTIR spectra of isatin and its 5-substituted analogues in the solid state were reported recently [19]. Authors' attempts to isolate solid alkali isatinates for the purpose of spectral comparison with the theoretical results for isatinato anion were unsuccessful [19].

We report in the present paper the experimental infrared spectrum of isatin azanion and determine the spectral and structural changes, arising from the conversion of isatin into the corresponding azanion by means of both quantitative IR spectra and DFT calculations.

EXPERIMENTAL

The isatin azanion (counter ion Na⁺) was prepared by adding 0.09 and 0.2 mol·l⁻¹ solutions of the parent isatin in DMSO-d₆ to excess of dry alkali-metal methoxide-d₃, obtained by reacting CD₃OD (Merck, 99% at enrichment), under argon. The con-

* To whom all correspondence should be sent:
E-mail: ev@orgchm.bas.bg

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 polar 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 CaF₂ 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 IR 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 ($VZPE$) 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 $ZPVE$ -corrected total energies ($E_{corr.}^{tot.}$) of the azanion and molecule: $\Delta E_{corr.}^{tot.} = E_{corr.}^{tot.}(\text{anion}) - E_{corr.}^{tot.}(\text{molecule})$ (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 ΔG_{acid} and DMSO pKa values for 97 C–H acids of various structures [38]. We have recently found a linear correlation between B3LYP/6-31++G** $\Delta E_{corr.}^{tot.}$ and pKa (solvent DMSO) for a series of C–H, N–H and O–H acids containing cyano and/or carbonyl groups [33]: $pK_a(\text{DMSO}) = 0.11507 \Delta E_{corr.}^{tot.} [\text{kJ}\cdot\text{mol}^{-1}] - 150.04$.

This equation has successfully been used to estimate pKa's of moderate [33, 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 (H₂O) [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** $\Delta E_{corr.}^{tot.}$ of 1400.1 kJ·mol⁻¹ (Table 1 the last line), we can calculate 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
$\Delta E_{corr.}^{tot.} = E_{corr.}^{tot.}(\text{azanion}) - E_{corr.}^{tot.}(\text{molecule})$			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 IR 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 $9\text{--}20$ and $9\text{--}24\text{ cm}^{-1}$, 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:

- $\nu_{\text{N-H}}$ at 3444 cm^{-1} (solvent carbon tetrachloride) corresponds to hydrogen-bond free N–H groups.

The $\nu_{\text{N-H}}$ band (solvent DMSO) is broad and complex, due to the formation of strong N–H...O=S hydrogen bonds between isatine and solvent.

- carbonyl stretchings $\nu_{\text{C=O}}$ at 1740 cm^{-1} with shoulder at 1757 cm^{-1} correspond to $\alpha\text{-C=O}$ and $\beta\text{-C=O}$ 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 $\nu(\alpha\text{-C=O})$ coordinate is predominant. The lower-frequency mode corresponds to the symmetrical stretch of the same fragment; in this case $\nu(\beta\text{-C=O})$ coordinate is predominant.

- The $\delta_{\text{N-H}}$ coordinate is strongly delocalized, taking part in vibrations Nos. 12–15 of isatin (Table 2).

Table 2. Theoretical (SCRF model) and experimental (DMSO- d_6) IR data for isatin.

No.	B3LYP/6-31++G**			Approximate Description ^a	Experimental data ^b	
	N, cm^{-1}	N, $\text{cm}^{-1\text{c}}$	A, $\text{km}\cdot\text{mol}^{-1}$		N, cm^{-1}	A, $\text{km}\cdot\text{mol}^{-1}$
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	$\nu_{\alpha\text{-(C=O)}}, \nu_{\beta\text{-(C=O)}}$	1757	68.8
7.	1789	1736	877.9	$\nu_{\beta\text{-(C=O)}}, \nu_{\alpha\text{-(C=O)}}$	1740	216.8
8.	1657	1612	693.6	$\nu_{\text{Ph}}, \nu_{\text{PhH}}, \delta_{\text{PhNC}}$	1621	110.2
9.	1639	1596	94.3	$\nu_{\text{Ph}}, \delta_{\text{PhH}}$	1611	12.1
10.	1517	1482	40.4	$\delta_{\text{PhH}}, \nu_{\text{Ph}}$	1487	3.1
11.	1500	1466	147.8	$\delta_{\text{PhH}}, \nu_{\text{Ph}}$	1470	43.5
12.	1408	1380	73.6	$\delta_{\text{NH}}, \delta_{\text{PhH}}, \delta_{\text{CNC}}$	1398	2.2
13.	1359	1334	110.0	$\nu_{\text{Ph}}, \delta_{\text{NH}}, \delta_{\text{PhH}}, \delta_{\text{PhNC}}$	1328	28.2
14.	1310	1289	76.2	$\nu_{\text{Ph}}, \delta_{\text{NH}}, \delta_{\text{PhH}}, \delta_{\text{PhNC}}$	1289	12.1
15.	1265	1246	19.0	$\delta_{\text{NH}}, \delta_{\text{PhH}}, \delta_{\text{PhNC}}$	1218	8.3
16.	1215	1200	25.1	$\delta_{\text{PhH}}, \nu_{\text{Ph}}, \delta_{\text{PhCC}}$	1199	11.9
17.	1205	1190	106.4	$\delta_{\text{NCC}}, \delta_{\text{PhH}}, \delta_{\text{Ph}}$	1189	10.5
18 ^f .	1175	1162	51.8	$\delta_{\text{Ph}}, \delta_{\text{PhH}}, \delta_{\text{NCC}}$	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 $\nu_{\text{exp}}=0.9343 \nu_{\text{theor}} + 64.45\text{ (cm}^{-1}\text{)}$; 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-d₆) IR data for isatin azanion.

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	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	$\nu_{\beta-(C=O)}$	1716	119.3
6.	1682	1636	206.1	$\nu_{\alpha-(C=O)}, \nu_{Ph}, \delta_{PhNC}, \delta_{PhH}$	1648	74.3
7.	1621	1579	1186.7	$\nu_{Ph}, \delta_{PhH}, \delta_{CCC}, \nu_{\alpha-(C=O)}$	1600	248.6
8.	1593	1553	1011.6	$\nu_{Ph}, \delta_{PhH}, \delta_{CCN}$	1568	134.7
9.	1503	1468	200.8	$\delta_{Ph}, \delta_{PhH}$	1470	61.7
10.	1463	1431	356.9	$\delta_{PhH}, \delta_{Ph}$	1439	92.7
11.	1341	1318	140.3	$\delta_{PhH}, \delta_{Ph}$	1320	42.5
12.	1330	1307	407.4	$\delta_{PhH}, \delta_{PhNC}$	1291	31.1
13.	1262	1244	112.4	$\delta_{PhNC}, \delta_{PhH}, \delta_{Ph}$	1243	16.5
14.	1244	1227	225.3	$\delta_{PhNC}, \delta_{PhH}, \delta_{Ph}$	1224	18.7
15.	1199	1185	3.1	$\delta_{PhH}, \delta_{PhCC}, \delta_{Ph}$	1210	13.8
16 ^d .	1153	1142	181.8	$\delta_{PhH}, \delta_{Ph}, \nu_{NCC}$	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):

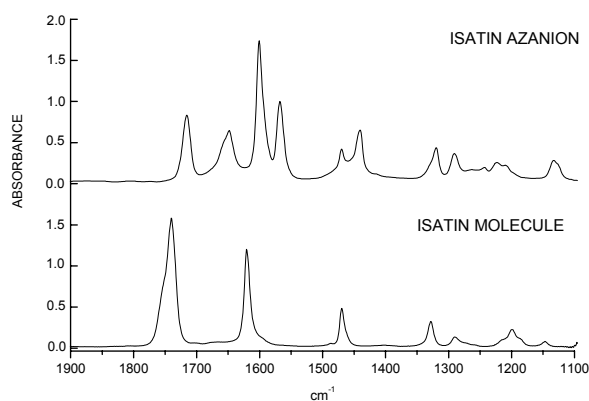


Fig. 1. IR spectra of isatin and isatin azanion in DMSO-d₆ (0.09 mol·l⁻¹)

- 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 lower-frequency vibrations (cf. above).

- Due to the strong direct resonance between the α -carbonyl group and azanionic center $\nu_{\alpha-C=O}$ frequency undergoes an essential lowering: calculated 121 cm⁻¹, measured 109 cm⁻¹. The computations

predict participation of $\nu_{\alpha-C=O}$ 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.

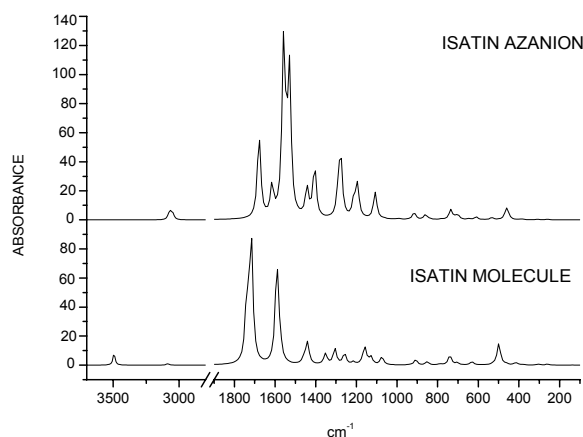


Fig. 2. Theoretical (B3LYP 6-31++G**, SCRF) IR spectra of isatin and isatin azanion.

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: $m.a.d. = n^{-1} \sum |R_i(\text{theor}) - R_i(\text{exp.})|$ of 0.0408 Å and $m.a.d. = n^{-1} \sum |A_i(\text{theor}) - A_i(\text{exp.})|$ of 0.71°.

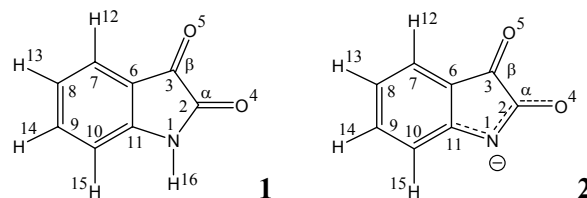
Table 4. Theoretical and experimental bond lengths R (Å) and angles A (°) in the isatin molecule and its azanion.

	B3LYP/6-31++G**			X-ray ^a
	molecule	azanion	Δ theor.(ion-mol)	
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	1.3903
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
<i>m.d.a.</i> ^c	<i>0.0408</i>			
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	123.62
A(2,4,6)	104.89	103.0657	-1.8338	104.92
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
<i>m.d.a.</i> ^c	<i>0.71</i>			

^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-

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**.

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 N¹C¹¹ and N¹C² bonds and strong lengthenings of the C²O³ and C⁶C¹¹ bonds.

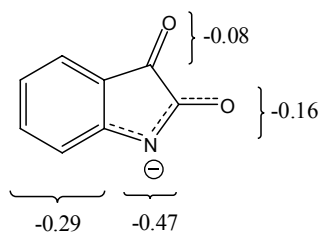
Bond lengthenings take place of the C²C⁴ and C⁴O⁵ bonds. The C²C⁴ bond in isatin (Table 4) is one of the longest α -dicarbonyl bond reported [15, 16] and probably responsible for cleavage of the five-membered ring in alkali media.

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 the 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	$q(\text{molecule})$	$q(\text{azanion})$
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 $\Delta q_i = q_i(\text{anion}) - q_i(\text{molecule})$ are quite informative to show the distributions of the new (carbanionic, azanionic, *ect.*) electric charges in anions [23–29] (and references therein). We can see in Scheme 2, that according to the computations $0.08e^-$, $0.16e^-$ and $0.29e^-$ of the new azanionic charge are delocalized over the β -carbonyl group, α -carbonyl group and phenylene ring, respectively, and $0.47e^-$ 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 predictions for the azanion **2** should also be adequate.

Acknowledgements: The financial support by the Bulgarian National Science Fund under contract Chem.-1510 is gratefully acknowledged.

REFERENCES

- O. Erdmann, *J. Prakt. Chem.*, **24**, 1 (1841).
- T. Sandmayer, *Helv. Chim. Acta*, **2**, 234 (1919).
- V. Glover, J. M. Halket, P. J. Watkins, A. Clone, B. L. Goodwin, M. Sandler, *J. Neurochem.*, **51**, 656 (1988).
- S. K. Bhattacharya, V. Glover, I. McIntyre, G. Oxenkrug, M. Sandler, *Neurosci. Lett.*, **92**, 218 (1982).
- S. K. Bhattacharya, S. K. Mitra, S. B. Acharya, *J. Psychopharmacol.*, **5**, 202 (1991).
- A. Cane, M. C. Tournaire, D. Barritault, M. Crumeyrolle-Arias, *Biochem. Biophys. Res. Commun.*, **276**, 379 (2000).
- The Merck Index, 13 Edn., Merck & Co. Inc., Whitehouse Station, N.J., USA, 2001.
- A. A. Jarrahpour, D. Khalili, *Molbank*, M437 (2005).
- S. N. Pandeya, D. Sriram, G. Nath, E. De Clercq, *Arzneimittel Forschun./Drug Res.*, **50**, 55 (2000).
- S. K. Sridhar, S. N. Pandeya, J. P. Stables, S. K. Armes, *Eur. J. Pharm. Sci.*, **16**, 129 (2002).
- A. M. A. Hassaan, *Transit. Met. Chem.*, **15**, 283 (1990).
- A. Garcia-Raso, J. J. Fiol, E. Molins, A. M. Calafat, P. A. Marzilli, L. G. Marzilli, *Metal-Based Drugs*, **2**, 81 (1995).
- P. Naumov, F. Atanasova, *Bull. Chem. Technol. Macedonia*, **19**, 1 (2000).
- G. H. Goldschmidt, F. J. Llewellyn, *Acta Crystallogr.*, **3**, 294 (1950).
- M. H. Palmer, A. J. Blake, R. O. Gould, *Chem. Phys.*, **115**, 219 (1987).
- M. A. Frolova, V. N. Kravtsov, V. N. Biyushkin, Y. M. Chumakov, O. N. Belkova, T. I. Malynovskii, *Zh. Strukt. Khim.*, **29**, 155 (1988).
- A. Bigatto, V. Galasso, *Spectrochim. Acta*, **35 A**, 725 (1979).
- B. N. Narziev, N. Mulloev, *J. Struct. Chem.*, **40**, 481 (1999).
- P. Naumov, F. Atanasova, *Spectrochim. Acta*, **57 A**, 469 (2001).
- I. N. Juchnovski, I. G. Binev, in: *The Chemistry of Functional Groups, Suppl. C*, S. Patai, Z. Rappoport (Eds), Wiley, New York, 1983, Ch. 4.
- V. Ognyanova, J. Petrov, G. N. Andreev, *Spectrosc. Lett.*, **30**, 933 (1997).
- G. N. Andreev, O. K. Argirov, V. Ognyanova, *J. Mol. Struct.*, **516**, 238 (2000).
- I. G. Binev, P. J. Vassileva-Boyadjieva, Y. I. Binev, *J. Mol. Struct.*, **447**, 235 (1998).
- Y. I. Binev, Ch. T. Petkov, L. Pejov, *Spectrochim. Acta Part A*, **56**, 1949 (2000).
- P. J. Vassileva-Boyadjieva, E. A. Velcheva, Y. I. Binev, *Bulg. Chem. Commun.*, **37**, 313 (2005).
- M. K. Georgieva, P. N. Angelova, I. G. Binev, *J. Mol. Struct.*, **692**, 23 (2004).
- D. Popova, M. K. Georgieva, O. I. Petrov, K. V. Petrova, E. A. Velcheva, *Int. J. Quant. Chem.*, **107**, 1752 (2007).
- L. I. Daskalova, E. A. Velcheva, I. G. Binev, *J. Mol. Struct.*, **826**, 198 (2007).
- E. A. Velcheva, B. A. Stamboliyska, *J. Mol. Struct.*, (2007) in press.
- 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. Nanayakkara, 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.
- A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).
- 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.*, **2**, 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

Посветена на акад. Иван Юхновски по повод на 70-та му годишнина

Постъпила на 17 декември 2007 г.; Преработена на 25 януари 2008 г.

(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 същевени спектрални промени. Същия теоретичен метод дава добро описание на пространствената и електронна структура на изатина. Според изчисленията, $0.76e^-$ (NBO) от новия (азанионен) заряд на аниона е делокализиран в ароматния остатък и азанионния център.