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IR spectra and structure of 1-H-isoindole-1,3(2H)-dione (phthalimide), *cis*-hexahydro-1-H-isoindole-1,3(2H)-dione (hexahydrophthalimide) and of their nitranions

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Abstract

The spectral and structural changes, accompanying the conversions of 1-H-isoindole-1,3(2H)-dione (phthalimide) and its *cis*-hexahydro derivative into the corresponding nitranions have been observed through IR spectra. These conversions lead to a strong decrease in carbonyl stretching frequencies ν_{CO}^{s} by 74 cm^{-1} and ν_{CO}^{as} by 134 cm^{-1} (mean values), a two-fold increase in the ν_{CO} spliting, etc. According to ab initio MO calculations, greater parts of anionic charges are delocalized within carbonyl groups. The alkali–metal derivatives of the imides studied mainly exist in the dimethyl sulphoxide as free solvated ions. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phthalimide (**1** in Scheme 1) is a starting material for numerous organic syntheses. As early as 1887 potassium phthalimide (**1A**, M = K) was used for the preparation of primary amines via alkylphthalimides (Gabriel's reaction) [1,2]. To begin with the pioneering work by Chouteau [3], we found in the literature 33 studies on the vibrational spectra of phthalimide. Most of these deal with the carbonyl ν_{CO} and/or imido ν_{NH} stretching bands, as well as the formation of hydrogen bonds between these groups and with the solvent, e.g. Refs. [4–11] (and the references therein). There are also present detailed assignments of the IR and Raman bands of phthalimide [12–15], based on the normal coordinate analysis [12,14,15]. The spectra of phthalimide nitranion (counter ions K^+ and Na^+) have also been studied repeatedly [12,16–18]; all the authors have found that the ν_{CO} frequencies of the anion are essentially lower than those of the parent phthalimide molecule [12,16–18]. Qualitatively similar strong ν_{CO} decreases have recently been found to accompany the conversions of other carboximides, viz. succinimide [19] and *o*-sulfobenzimide (saccharin) [20,21] into nitranions and of carboxamides into anions [22–25] and dianions [23,24]. The IR spectrum of *cis*-hexahydrophthalimide has not been studied in detail [26] and its nitranion has not been measured.

The structures of the phthalimide molecule [15,17,18,27] and of its nitranion [18,28] have been studied by Hückel's and semiempirical methods. The crystal and molecular structures of phthalimide and potassium phthalimide have been determined by

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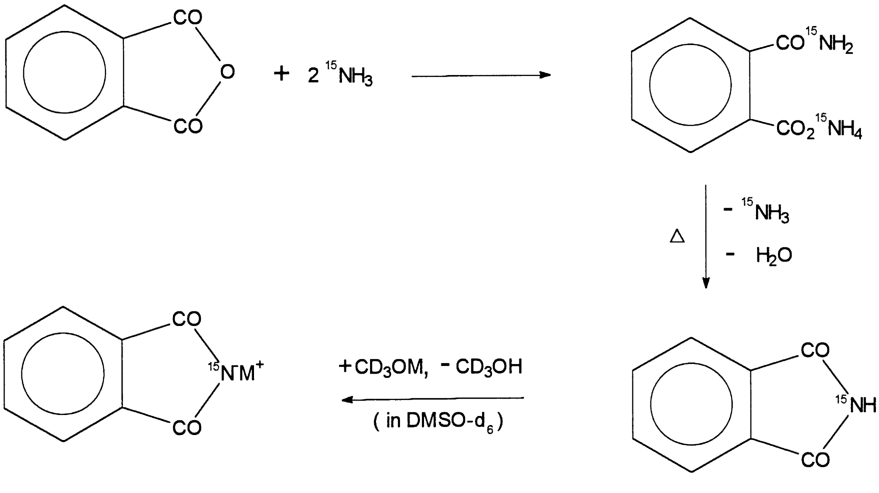


1A, M = Na and K **1**

Scheme 1. Preparation of phthalimide-^{15}N (**1**) and of its alkali–metal derivatives (**1A**).

Matzat [29] and Nagel et al. [30], respectively, on the basis of X-ray diffraction, and the dipole moments of phthalimide [31] and hexahydrophthalimide [26] were determined in dioxan by Lee and Kumler quite a long time ago.

In the literature we have found neither the qualitative IR data, nor ab initio force-field calculations of the title species. Combined IR/ab initio studies in a series of imides [19,21], amides [23–25] and their nitranions [19,21,24], carbanions [23,25] and dianions [23,24] have proved to be useful in studying the changes in the parent molecules, caused by their conversions into anions. Hence, the purpose of the present study is to follow the spectral and structural changes, which take place during the course of the conversions of phthalimide and its hexahydro derivative into the corresponding nitranions on the basis of both, quantitative IR spectra and ab initio force-field calculations.

2. Experimental

Commercial phthalimide (Fluka) was recrystallized from dry ethanol. Phthalimide–^{15}N was prepared by reacting phthalic anthydride with aqueons $^{15}NH_3$ (Isocomerz, 95% at. enrichment), followed by the evaporation of the water and sublimation of the residue. The sublimate (phthalimide–^{15}N, **1** in Scheme 1) was recrystallized from dry ethanol to show a m.p. of 238°C, in agreement with Ref. [32]. *Cis*–hexahydrophthalimide was prepared in a similar way from the corresponding anhydride (Fluka) and $^{14}NH_4$ aq.; m.p.136°C in agreement with Ref. [32]. Dry sodium and potassium methoxides-d_3 were prepared by reacting the metals with methanol-d_4 (Merck), followed by removing the excess of alcohol in vacuo. The nitranions (counter ions Na^+ and K^+) of the phthalimide, phthalimide–^{15}N (1A in Scheme 1) and *cis*-hexahydrophthalimide were prepared by adding DMSO and DMSO-d_6 solutions of the parent imides to an excess of dry alkali metal methoxides-d_3. The metallation was practically complete: no bands of the parent imides were seen in the spectra after metalation, as 1,2-dicarboximides are moderately weak acids, e.g. pK_a of phthalimide and succinimide are 13.4 and 14.6 (solvent DMSO), respectively [34].

The IR spectra were recorded on Bruker IFS 113v and Vector 22 FTIR spectrometers in a CaF_2 cell of 0.13 mm path length (for DMSO and DMSO-d_6 solutions, concentrations 0.02–0.16 mol l^{-1}), a KBr cell of 1 mm path length (for the $CDCl_3$ solutions, concentration 0.02–0.07 mol l^{-1}), and KBr and CsI discs, at a resolution of 1 cm^{-1} and 50 scans. The integrated intensities were measured after having decomposed

Table 1
Theoretical (HF/6-31G) and experimental (DMSO/DMSO-d_6 solutions) infrared data for the phthalimide molecule

No.	Ab Initio force field					Experimental[a]		
	ν (cm^{-1})	ν[b] (cm^{-1})	Δ[c]	A (km mol^{-1})	Approximate description[d]	ν (cm^{-1})	Δ[c]	A (km mol^{-1})
1	3937	3516	−8.2	127.8	100 ν_{CH}	3429[e]	−7.4	81.6
2	3388	3025	0.0	13.0	99 ν_{PhH}	3088[e]	1.2	1.0
3	3380	3018	0.0	4.4	99 ν_{PhH}	3061[e]	−1.5	8.2
4	3368	3009	0.0	5.8	99 ν_{PhH}	2977[e]	1.5	0.8
5	3355	2996	0.0	1.7	99 ν_{PhH}			
6	1983	1771	−0.1	164.5	80 ν^{s}_{CO}, 13 δ_{HNC}	1769	−0.5	35.3
7	1937	1729	−1.7	905.9	74 ν^{as}_{CO}, 12 δ_{NCC}	1727	−0.9	368.5
8	1822	1627	0.0	13.9	63 ν_{CC}, 25 δ_{CCC}	1607	−0.4	7.8
9	1797	1604	0.0	2.2	97 ν_{CC}			
10	1646	1469	0.0	13.0	52 δ^{ip}_{PhH}, 42 ν_{CC}	1467	0.0	6.0
11	1642	1466	0.0	4.8	57 δ^{ip}_{PhH}, 30 δ_{CCC}, 11 ν_{CC}	1424	−1.1	0.9
12	1526	1363	−12.8	4.6	71 δ_{HNC}, 16 ν_{CO}			
13	1489	1330	−3.2	204.9	36 ν_{CC}, 20 δ_{HNC}, 14δ_{NCO}	1376	−1.3	57.4
14	1459	1303	0.0	1.3	68 δ^{ip}_{PhH}, 20 δ_{CCC}	1341	−0.7	2.9
15	1404	1254	−6.8	151.3	30 δ^{ip}_{PhH}, 30 ν_{CC}, 22 ν_{CN}	1304	−6.5	37.0
						1206	−1.0	4.7
16	1321	1179	−1.8	40.2	27 δ_{CCC}, 23 ν_{CN}, 21 ν_{CC}, 18 δ^{ip}_{PhH}	1181	−2.0	12.8
17	1291	1153	−0.8	5.0	50 δ^{ip}_{PhH}, 36 ν_{CC}, 13 ν_{CN}	1142	−4.1	3.3
18	1262	1127	−3.4	0.0	42 δ_{CCC}, 39 ν_{CC}			
19	1213	1083	−1.2	29.0	50 δ_{CCC}, 20 ν_{CC}, 13 ν_{CN}	1089[e]	−0.5	8.4
20	1200	1027	0.0	0.0	80δ^{oop}_{PhH}, 14τ_{CCCC}	1069[e]	−0.5	2.7
21	1181	1055	−7.3	79.6	46 ν_{CN}, 32 δ_{CCC}, 15 δ_{CNC}	1036[e]	−6.1	45.2
22	1154	1030	0.0	1.2	90 δ^{oop}_{PhH}	1010[e]	−0.6	0.3
23	1112	993	−0.3	0.3	60 δ_{CCC}, 16 ν_{CC}	977[f]	−0.4	vw
24	1064	950	0.0	0.0	100 δ^{oop}_{PhH}			
25	927	827	−1.6	0.4	95 δ^{oop}_{PhH}	818[f]	−3.0	vw
26	912	814	0.0	0.0	100 τ_{NCCC}	804[f]	0.0	vw
27	893	797	−1.9	3.6	32 δ_{NCC}, 32 δ_{CCC}, 12 ν_{CC}	794[f]	−0.7	w
28	844	754	−3.7	329.8	82 τ_{HNCO}	745[f]	−4.3	w
29	820	732	−3.3	3.5	69 ν_{CC}, 28 δ_{NCC}	714[f]	−2.3	m
30	748	668	0.0	0.0	60 τ_{CCCC}, 32 τ_{HNCO}			
31	729	651	−3.3	1.8	61 δ_{NCO}, 30 δ_{CCC},			
32	719	642	−0.4	65.7	100 τ_{HNCC}	668[f]	0.0	m
33	710	634	−3.6	19.3	50 δ_{HNC}, 14 δ_{CCC}	649[f]	−6.0	m
						559	−1.0	64.2
34	605	540	−3.7	11.3	41 δ_{CCC}, 26 ν_{CN}	546[e]	−3.1	4.5
35	597	533	−0.4	11.8	50 δ_{CCC}, 26 δ_{NCC}	529[e]	−0.4	6.4
36	525	469	0.0	0.0	60 τ_{CCCC}, 26 τ_{HNCO}			
37	476	425	−0.2	3.5	90 τ_{CCCC}	408[f]	0.3	vw
38	370	330	−0.2	26.0	56 δ_{NCO}, 24 δ_{HNC}	359[f]	−0.3	m
39	267	238	0.0	0.5	68 δ_{CCC}, 22 δ_{NCO}	270[g]	−0.8	m
40	218	195	−0.7	6.8	52 τ_{CCCC}, 35τ_{HNCC}	210[g]	−2.2	m
41	192	172	−1.0	5.5	60 τ_{HNCC}, 22τ_{CCCC}	175[g]	−2.3	s
42	150	139	0.0	0.0	64 τ_{NCCC}, 20 τ_{HNCO}	–		

[a] Measured after having decomposed the complex bands into components. Relative intensities: s, strong; m, medium; w, weak; vw, very weak.

[b] Scaled by 0.8929 [36].

[c] Calculated and meashured ^{15}N isotopic shifts $\Delta = \nu_{labelled} - \nu_{non\text{-}labelled}$.

[d] Vibrational modes: ν, stretching; δ, deformation (all kinds of); τ, torsion; superscripts: s, symmetrical; as, asymmetrical; ip, in-plane; oop, out-of-plane; subscript sk, skeletal. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the energy distribution matrix [33].

[e] Solvent $CDCl_3$.

[f] Solid, in KBr disc.

[g] Raman data, solvent DMSO [15].

Table 2
Theoretical (HF/6-31G) and experimental (DMSO/DMSO-d_6 solutions) infrared data for the *cis*-hexahydrophthalimide molecule

No	Ab initio force field				Experimental[a]	
	ν (cm^{-1})	ν[b] (cm^{-1})	A (km mol^{-1})	Approximate description[c]	ν (cm^{-1})	A (km mol^{-1})
1	3873	3458	97.5	$100\nu_{NH}$	3407[d]	54.9
2	3278	2927	31.7	$74\nu^{as}_{CH_2}$ $25\nu_{NH}$	2947[d]	57.2
3	3260	2911	7.3	$73\nu_{CH}$, $25\nu^{s}_{CH_2}$	2927[d]	5.8
4	3254	2905	57.6	$94\nu^{as}_{CH_2}$	2914[d]	14.4
5	3243	2896	51.9	$74\nu^{as}_{CH_2}$, $12\nu^{s}_{CH_2}$	2877[d]	4.1
6	3237	2890	22.6	$76\nu^{as}_{CH_2}$, $22\nu^{s}_{CH_2}$		
7	3200	2857	37.0	$88\nu^{s}_{CH_2}$	2862[d]	
8	3196	2854	8.0	$96\nu^{s}_{CH_2}$		
9	3184	2843	31.7	$80\nu^{s}_{CH_2}$,$14\nu_{CH}$		
10	3167	2828	25.6	$95\nu^{s}_{CH_2}$		
11	3161	2822	10.7	$84\nu^{s}_{CH_2}$ ν^{s}_{CO},ν^{as}_{CO}		
12	1960	1750	86.9	$82\nu^{s}_{CO}$, $16\delta_{CNC}$	1772	35.3
13	1914	1709	851.2	$73\ \nu^{as}_{CO}$, $10\delta_{HNC}$	1712	341.0
14	1664	1486	6.6	$97\delta_{CH_2}$ (scissoring)		
15	1657	1479	12.8	$99\delta_{CH_2}$(scissoring)	1451	10.0
16	1652	1475	3.8	$91\delta_{CH_2}$(scissoring)		
17	1646	1470	6.9	$94\delta_{CH_2}$(scissoring)		
18	1548	1382	3.9	$70\delta_{CH_2}$, $17\delta_{HCC}$		
19	1539	1374	14.6	$64\delta_{HNC}$, $18\nu_{CO}$	1393	2.1
20	1535	1371	0.3	$92\delta_{CH_2}$		
21	1528	1365	1.7	$93\delta_{CH_2}$	1365	10.1
22	1521	1358	3.2	$88\delta_{CH_2}$	1354	1.4
23	1498	1338	29.3	$44\delta_{HCC}$, $31\delta_{CH_2}$	1339	14.8
24	1478	1320	5.3	$53\delta_{HCC}$, $33\delta_{CH_2}$	1333	5.5
25	1465	1308	6.7	$53\delta_{CH_2}$, $35\delta_{HCC}$		
26	1454	1299	150.1	$70\delta_{CNC}$, $19\delta_{OCC}$	1317	23.2
27	1427	1274	9.2	$48\delta_{CH_2}$, $20\delta_{HCC}$, $10\nu_{CC}$	1263	1.7
28	1396	1246	2.1	$71\delta_{CH_2}$, $21\delta_{HCC}$,	1249	6.0
29	1391	1242	12.9	$55\delta_{HCC}$, $20\delta_{CH_2}$,$10\nu_{CC}$	1233	4.0
30	1346	1202	88.4	$33\delta_{CH_2}$, $30\nu_{CN}$,$19\delta_{HCC}$	1190	26.1
31	1322	1180	71.2	$32\delta_{CH_2}$, $30\nu_{CN}$, $20\delta_{CCC}$	1173	26.5
32	1272	1136	8.2	$63\delta_{CH_2}$, $21\tau_{CCCC}$	1136	7.2
33	1234	1102	0.3	$45\nu_{CC}$, $27\delta_{HCC}$, $19\delta_{CH_2}$	1114	1.4
34	1218	1088	29.9	$41\nu_{CC}$, $22\nu_{CN}$,$18\delta_{CH_2}$	1074	12.2
35	1164	1039	8.3	$42\delta_{CH_2}$, $37\nu_{CC}$	1047	5.8
36	1155	1032	1.7	$66\nu_{CC}$, $22\delta_{CH_2}$	1034	1.0
37	1119	999	4.9	$38\delta_{CCC}$, $33\delta_{CH_2}$,$15\ \nu_{CN}$	1000	4.2
38	1045	933	11.1	$45\delta_{CH_2}$, $27\delta_{CCC}$, $19\nu_{CC}$	937[e]	m
39	1030	920	19.8	$75\nu_{CC}$, $22\nu_{CN}$	893[e]	vw
40	978	873	3.9	$47\nu_{CC}$, $28\delta_{CH_2}$	881[e]	vw
41	968	865	0.9	$51\delta_{CCC}$, $25\nu_{CC}$, $23\delta_{CH_2}$	841[e]	m
42	923	824	2.7	$49\nu_{CC}$, $24\delta_{CCC}$, $15\delta_{CH_2}$	820[e]	w
43	897	801	133.5	$25\tau_{NCCC}$, $21\tau_{HNCC}$, $24\delta_{OCC}$	797[e]	vw
44	876	782	1.8	$51\delta_{CH_2}$, $41\nu_{CC}$,	784[e]	w
45	829	740	67.8	$40\tau_{HNCC}$, $23\nu_{CC}$, $19\delta_{CCC}$	743[e]	w
46	802	716	12.6	$56\ \nu_{CC}$, $16\delta_{OCC}$	716[e]	w
47	753	673	32.8	$45\tau_{OCCC}$	643[e]	vw
48	698	623	2.4	$45\delta_{CCC}$, $40\nu_{CC}$	605[d]	8.7
49	665	593	6.4	$73\delta_{NCC}$, $20\delta_{OCC}$	586[d]	2.4
50	622	555	15.3	$53\delta_{NCC}$, $23\nu_{CC}$	564[d]	11.5

Table 2 (*continued*)

No	Ab initio force field				Experimental[a]	
	ν (cm^{-1})	ν[b] (cm^{-1})	A (km mol^{-1})	Approximate description[c]	ν (cm^{-1})	A (km mol^{-1})
					550[d]	1.7
51	578	516	4.7	$36\tau_{CCCC}$, $30\delta_{OCC}$	532[d]	2.6
					449[d]	1.1
52	490	438	1.3	$76\delta_{CCC}$	428[d]	2.0
53	455	406	14.4	$33\ \delta_{CNC}$, $32\delta_{CCO}$, δ_{CCC}	421[e]	3.2
54	392	350	19.6	$40\delta_{CCC}$, $33\delta_{CCO}$, $18\delta_{CNC}$	375[f]	w
55	353	315	1.3	$46\tau_{CCCC}$, $25\tau_{CCCH}$	344[f]	vw
56	283	253	3.2	$64\tau_{CCCC}$, $14\tau_{CCCH}$	270[f]	vw
57	238	216	0.5	$72\tau_{CCCC}$, $15\tau_{CCCO}$	238[f]	vw
58	181	162	15.4	$59\tau_{CCCO}$, $38\tau_{CCCN}$	179[e]	w
59	141	126	0.9	$86\tau_{CCCC}$		
60	85	76	0.3	$76\tau_{CCCC}$, $21\tau_{CCCO}$		

[a] Measured after having decomposed the complex bands into components. Relative intensities: s, strong; m, medium; w, weak; vw, very weak.

[b] Scaled by 0.8929 [36].

[c] Vibrational modes: ν, stretching; δ, deformation (all kinds of); τ, torsion; superscripts: s, symmetrical; as, asymmetrical; ip, in-plane; oop, out-of-plane; subscript sk, skeletal. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the energy distribution matrix [33].

[d] Solvent $CDCl_3$.

[e] Solid, in KBr.

[f] Solid, in CsI.

the complex bands into components by using the OPUS 2.0 program, which is a part of the Bruker's software. The fitting procedure was carried out for all the bands, in order to account for their baselines and real widths. The spectra of the nitranions studied do not depend on the counterion (Na^+ or K^+) thus these derivatives exist in DMSO as kinetically free solvated ions mainly, like those of succinimide [19] and *o*-sulfobenzimide [21] etc.

3. Computations

The ab initio force-field computations have been performed using the GAMESS software [35] (AIX version, 1995) at the RHF 3-21 and 6-31G levels. As we have recently found in the case of succinimide [19], the enlargement of the latter basis set by including polarisation and diffuse functions leads to some deterioration rather than improvement of the results. No scaling in the ab initio force field has been done.

4. Results and discussion

4.1. Infrared spectra

Considering first the IR spectra of the species studied will make it possible to follow the spectral changes caused by the conversion of the molecules studied into the corresponding nitranions.

4.1.1. Molecules

The IR spectra of the molecules studied are quite similar, but the obvious difference between them is in the ν_{CH} region: the presence of four methylene groups in the hexahydrophthalimide molecule gives rise to moderate $\nu^{as}_{CH_2}$ and $\nu^{s}_{CH_2}$ bands, whereas the ν_{PhH} bands of phthalimide are much weaker. There is a good agreement between experimental and scaled theoretical frequencies of the molecules studied (Tables 1 and 2). The mean deviation between them is 21 cm^{-1} for phthalimide and 14 cm^{-1} for its hexahydro derivative. These values lie within the interval of 14–30 cm^{-1} of mean deviations, typical for molecules containing carbonyl groups [19,21,23–25].

Table 3
Theoretical (HF/6-31G) and experimental (DMSO/DMSO-d_6 solutions, counter ion Na^+) infrared data for the phthalimide nitranion

No	Ab initio force field					Experimental[a]		
	ν (cm^{-1})	ν[b]	Δ[c]	A (km mol^{-1})	Approximate description[d]	ν (cm^{-1})	Δ[c]	A (km mol^{-1})
1	3361	3001	0.0	28.3	$99\nu_{PhH}$	3076	[e]	3.7
2	3355	2996	0.0	35.1	$99\nu_{PhH}$	3045	[e]	3.1
3	3333	2976	0.0	46.0	$99\nu_{PhH}$	3028	[e]	1.7
						3013	[e]	0.9
4	3311	2956	0.0	9.1	$99\nu_{PhH}$	2958	[e]	6.3
5	1916	1711	0.0	93.2	$72\nu^{s}_{CO}$, $16\nu_{CN}$	1699	−0.2	56.0
6	1823	1628	−0.2	242.7	$54\nu_{CC}$, $23\delta_{CCC}$	1612	−0.9	259.9
7	1797	1605	0.0	15.1	$90\nu_{CC}$	1569	0.0	76.4
8	1772	1582	−0.7	1163.2	$66\nu^{as}_{CO}$, $11\delta_{NCC}$	1591	−0.7	246.4
9	1632	1457	0.0	9.0	$56\delta^{ip}_{PhH}$, $30\nu_{CC}$	1493	[e]	5.1
10	1631	1456	0.0	8.8	$58\delta^{ip}_{PhH}$, $34\delta_{CCC}$	1457	[e]	4.9
						1369	−2.0	15.3
						1348	0.0	35.0
11	1449	1294	−0.9	128.2	$50\nu_{CC}$, $23\delta^{ip}_{PhH}$	1275	−9.5	100.4
12	1434	1280	−0.5	1.5	$67\delta^{ip}_{PhH}$, $15\ \delta$ccc	1236	−1.4	9.2
13	1361	1215	−9.2	263.3	$29\nu^{s}_{NC}$, $28\delta^{ip}_{PhH}$, $18\ \delta_{CNC}$	1206	−6.2	51.1
14	1322	1180	−12.2	205.7	$69\nu^{as}_{NC}$, $17\delta^{ip}_{PhH}$	1188	−2.4	31.5
15	1278	1141	−0.5	1.9	$46\delta^{ip}_{PhH}$, $46\nu_{CC}$	1178	−4.2	7.7
16	1249	1115	−7.9	64.1	$26\delta^{ip}_{PhH}$, $23\nu_{CC}$, $21\nu_{NC}$	1127	−9.1	65.4
17	1245	1112	−5.8	20.3	$42\nu_{CC}$, $20\delta^{ip}_{PhH}$	1094	[e]	4.0
18	1200	1071	−0.2	5.1	82δccc	1051[f]		w
19	1164	1039	0.0	0.0	$82\delta^{oop}_{PhH}$	1040[g]		vw
20	1124	1004	0.0	3.5	$92\delta^{oop}_{PhH}$	1006[f]		vw
21	1105	987	−0.2	7.1	$62\delta_{CCC}$, $17\delta^{ip}_{PhH}$	974[f]		vw
22	1038	927	0.0	0.0	$93\delta^{oop}_{PhH}$	951[f]		w
23	908	811	−2.8	19.6	$30\delta_{OCC}$, $24\delta_{NCC}$, $22\delta_{CCC}$	840[f]		m
						820[f]		vw
24	894	798	−0.7	24.6	$89\delta^{oop}_{PhH}$	799[f]		vw
25	875	781	0.0	0.0	$89\tau_{CCCC}$			
						769[f]		vw
						756[f]		vw
26	815	728	−3.0	0.8	$65\nu_{CC}$, $21\delta_{NCO}$	743[f]		vw
27	784	700	−3.6	128.5	$79\tau_{CCCC}$, $14\delta^{oop}_{PhH}$	717[f]		s
28	757	676	−2.4	1.4	54δocc, $34\delta_{CCC}$	688[f]		vw
29	751	671	0.0	0.0	$68\tau_{CCCC}$, $37\tau_{OCCC}$	664[f]		vw
30	716	639	−3.8	1.0	$55\delta_{CNC}$, $13\delta_{NCC}$, $15\nu_{NC}$	629[f]		w
31	612	546	−4.6	10.9	$38\delta_{CCC}$, $20\nu_{NC}$, $20\nu_{CC}$	573[f]		vw
						559		vw
32	592	529	−0.6	29.4	$56\delta_{CCC}$, $29\delta_{NCC}$	538[f]		m

Table 3 (*continued*)

No	Ab initio force field					Experimental[a]		
	ν (cm^{-1})	ν[b]	Δ[c]	A (km mol^{-1})	Approximate description[d]	ν (cm^{-1})	Δ[c]	A (km mol^{-1})
						416		vw
33	528	471	0.0	0.0	$64\tau_{CCCC}$, $24\tau_{NCCO}$			
34	483	431	−0.3	0.1	$98\tau_{NCCC}$	408[f]		vw
						399		vw
35	375	335	−0.1	16.3	$48\delta_{NCO}$, $26\ \delta_{CNC}$	364[f]		m
						340		vw
						269		vw
36	254	227	0.0	0.7	$68\delta_{CCC}$	208[f]		vw
37	223	199	−3.9	0.2	$40\tau_{CCCC}$, $30\tau_{NCCO}$	190[f]		m
38	201	179	−0.4	9.5	$60\tau_{NCCO}$, $36\tau_{CCCC}$	164[f]		m
39	148	132	0.0	0.0	$68\tau_{NCCC}$	156[g]		vw

[a] Measured after having decomposed the complex bands into components. Relative intensities: s, strong; m, medium; w, weak; vw, very weak.

[b] Scaled by 0.8929 [36].

[c] Solvent $CDCl_3$.

[d] Vibrational modes: ν, stretching; δ, deformation (all kinds of); τ, torsion; superscripts: s, symmetrical; as, asymmetrical; ip, in-plane; oop, out-of-plane; subscript sk, skeletal. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the energy distribution matrix [33].

[e] No reliable data.

[f] Hase's solid state IR data [12].

[g] Hase's solid state Raman data [12].

Table 4
Theoretical (HF/6-31G) and experimental (solvent DMSO/DMSO-$d_{6,}$ counter ion Na^+) infrad data for the *cis*-hexahydrophthalimide nitranion

No	Ab initio force field				Experimental[a]	
	ν (cm^{-1})	ν[b]	A ($km\ mol^{-1}$)	Approximate description[c]	ν (cm^{-1})	A ($km\ mol^{-1}$)
1	3254	2906	73.2	$90\nu^{as}_{CH_2}$	2937	83.1
2	3230	2884	38.6	$96\nu^{as}_{CH_2}$	2923	26.5
3	3221	2876	83.6	$92\nu^{as}_{CH_2}$	2898	13.9
4	3213	2869	46.6	$85\nu^{s}_{CH_2}$	2867	4.3
5	3207	2864	58.8	$58\nu^{s}_{CH_2}$, $36\nu^{as}_{CH_2}$		
6	3190	2848	84.2	$63\nu^{s}_{CH_2}$, $29\nu^{as}_{CH_2}$	2854	20.8
7	3176	2836	24.0	$52\nu^{s}_{CH_2}$, $41\nu^{as}_{CH_2}$		
8	3150	2813	67.4	$74\nu^{as}_{CH_2}$, $22\nu^{s}_{CH_2}$		
9	3138	2802	57.0	$94\nu^{s}_{CH_2}$		
10	3125	2790	30.5	$75\nu^{s}_{CH_2}$, $22\nu^{s}_{CH_2}$		
11	1883	1682	68.2	$74\nu^{s}_{CO}$, $18\delta_{CCC}$	1690	18.4
12	1746	1559	1381.3	$76\nu^{as}_{CO}$, $11\delta_{NCC}$	1580	549.7
13	1665	1486	14.7	$94\delta_{CH_2}$ (scissoring)	1460	2.5
14	1655	1478	11.7	$97\delta_{CH_2}$ (scissoring)	1449	5.2
15	1651	1474	1.9	$94\delta_{CH_2}$ (scissoring)		
16	1644	1468	16.2	$95\delta_{CH_2}$ (scissoring)	1435	3.1
17	1541	1376	2.6	$65\delta_{CH_2}$, $23\delta_{HCC}$		
18	1527	1364	2.5	$72\delta_{CH_2}$	1363	8.0
19	1522	1359	1.8	$90\delta_{CH_2}$		
20	1510	1348	0.7	$85\delta_{CH_2}$	1348	5.3
21	1491	1331	13.7	$58\delta_{HCC}$, $23\delta_{CH_2}$	1326	43.3
22	1477	1318	1.6	$45\delta_{HCC}$, $30\delta_{CH_2}$		
23	1463	1306	21.1	$48\delta_{CH_2}$, $22\delta_{HCC}$	1306	68.5
24	1419	1267	3.7	$62\delta_{CH_2}$, $15\tau_{HCCC}$		
25	1403	1253	231.4	$69\delta_{CNC}$, $16\delta_{OCC}$	1247	115.5
26	1387	1238	152.6	$50\nu_{CN}$, $24\tau_{HCCC}$	1224	11.6
27	1386	1237	74.8	$43\delta_{CH_2}$, $17\nu_{CN}$, $10\tau_{HCCC}$		
28	1358	1212	53.4	$37\tau_{HCCC}$, $20\delta_{CH_2}$,$14\nu_{CC}$	1211	12.7
29	1311	1171	19.6	$39\delta_{CH_2}$, $33\tau_{HCCC}$	1171	2.5
30[d]	1264	1129	9.4	$56\delta_{CH_2}$, $21\nu_{CC}$	1129	17.5

[a] Measured after having decomposed the complex bands into components. Relative intensities: s, strong; m, medium; w, weak; vw, very weak.

[b] Scaled by 0.8929 [36].

[c] Vibrational modes: ν, stretching; δ, deformation (all kinds of); τ, torsion; superscripts: s, symmetrical; as, asymmetrical; ip, in-plane; oop, out-of-plane; subscript sk, skeletal. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the energy distribution matrix [33].

[d] Followed by 27 low-frequency normal vibrations.

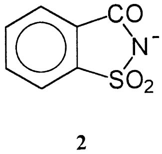
There is a fairly good agreement between calculated and measured ^{15}N isotopic shifts Δ (Table 1, cf. columns 4 and 8). The approximate description of the normal vibrations of phthalimide (Table 1) is not dissimilar from the band assignments of Hase [12] and Arenas et al. [15]; there are some differences in the case of certain low-frequency bands. In the literature we did not find any detailed band assignment of the IR spectrum of hexahydrophthalimide.

4.1.2. Nitranions

The IR spectra of the nitranions studied are not so similar than those of the corresponding molecules: essential differences are seen near 3000 and 1600 cm^{-1}. The theoretical and experimental IR data for the nitranions studied are compared in Tables 3 and 4. The mean deviation between experimental and scaled theoretical frequencies is 20 cm^{-1} for the phthalimide nitranion and 13 cm^{-1} for its hexadeutero derivative. So, the agreement between these values can be considered as very good, having in mind the interval of 16–49 cm^{-1} of mean deviations, found for anions and dianions containing carbonyl groups [19,21,23–25,34]. However the agreement between the calculated and measured ^{15}N isotopic shifts Δ for the phthalimide nitranion (Table 3, columns 4 and 8) is somewhat worse than in the previous case (cf. Table 1). The approximate description of most normal vibrations of the same anion (Table 3) agrees with Hase's assignments of vibrational bands of potassium phthalimide [12].

Special attention should be paid to the spectrum near 1600 cm^{-1}. As early as 1964 Matsuo [16] reported three almost equi-intense bands near 1600 cm^{-1} in the spectrum of the solid potassium phthalimide. The author assumed that $\nu_{\mathrm{CO}}^{\mathrm{as}}$ "is split into a triplet for some unknown reasons" [16]. Twenty-four years later Hase [12] confirmed the presence of these three bands, strong in the IR and medium in the Raman spectra. However, the author [16] assigned them, as follows: 1587 cm^{-1}, $\nu_{\mathrm{CO}}^{\mathrm{as}}$; 1596 cm^{-1}, ring stretch; 1610 cm^{-1}, ring stretch. We found that both potassium and sodium phthalimide show in DMSO only two equi-intense very strong bands, described in Table 3 as: 1591 cm^{-1}, $\nu_{\mathrm{CO}}^{\mathrm{as}}$ and 1612 cm^{-1}, ring vibration type 9a (Wilson's notation). Hence, Hase's assignment is confirmed unambiguously. However, the intensity of the 1612 cm^{-1} band is surprisingly high.

1. According to the theory the ν_{8a} band should be five-fold weaker than $\nu_{\mathrm{CO}}^{\mathrm{as}}$ (Table 3).
2. The fully analogous ν_{8a} band of the *o*-sulfobenzimide (saccharin) nitranion (Formula **2**) has only moderate intensity, 41.6 km mol^{-1}, and is four-fold weaker than ν_{CO} [21].
3. Very strong $\nu_{8a,b}$ bands are typical only for anions where the anionic center is directly bonded to the phenyl (phenylene) ring (Formula **3**) [24,35–41].

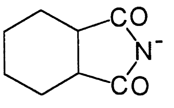


2

3: X = CN, $COCH_3$, $COOCH_3$, NO_2

Z = NC-HC^-, HN^-, O^-

However, the $\nu_{\mathrm{CO}}^{\mathrm{as}}$ band of phthalimide nitranion is weaker than expected on the basis of both theoretical data (Table 3, No. 8) and experimental results for *cis*-hexahydrophthalimide nitranion (Formula **4**, see Table 4, No.12) and succinimide nitranion (**5**).



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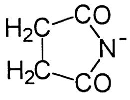
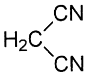


5: $A_{\mathrm{CO}}^{\mathrm{as}}$ = 657 km.mol^{-1}[19]

Hence, we think that in the case of the phthalimide nitranion there is an intensity borrowing from $\nu_{\mathrm{CO}}^{\mathrm{as}}$ to the ν_{9a} band.

In good agreement between the theory and the experiment, the conversion of both phthalimide and hexahydrophthalimide molecules into corresponding nitranion leads to strong spectral changes (cf. Tables 1–4), for example:

1. Strong decreases in $\nu_{\mathrm{CO}}^{\mathrm{s}}$ by 74 cm^{-1} and in $\nu_{\mathrm{CO}}^{\mathrm{as}}$ by 134 cm^{-1} (mean values for the two imides studied). We have recently found the corresponding values of 74 and 139 cm^{-1} in the case of succinimide [19]. Strong ν_{CO} decreases have been found to accompany the conversions of other imides [18,20,21], many amides [22–25] and many other carbonyl compounds [18,34,40,41] into anions and dianions.
2. Enlargement of ν_{CO} splittings $\Delta\nu_{\mathrm{CO}} = \nu_{\mathrm{CO}}^{\mathrm{s}} - \nu_{\mathrm{CO}}^{\mathrm{as}}$ from 51 to 109 cm^{-1} (mean values). The corresponding $\Delta\nu_{\mathrm{CO}}$ increase in the succinimide case is from 58 to 123 cm^{-1} [19]. For comparison the conversion of the malononitrile (Formula **6**) and its ylidene derivatives (**7**) into anions (**8**) leads to a 12- to 13-fold enlargement of the ν_{CN} splitting, from 4 cm^{-1} (calculated, but not measurable) to 49–54 cm^{-1} [41,42].



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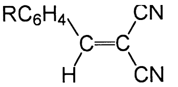
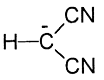


7: R = H and HO



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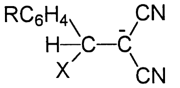


9: R = H and HO

X= CN and CH_3O

Table 5
Bond lengths (Å) and bond angles (deg.) of the phthalimide molecule and of its nitranion

Geometry parameters[a]	Molecule				Nitranion		
	X-ray[b]	MINDO/3[c]	3-21G	6-31G	X-ray[d]	3-21G	6-31G
$r(N^1–C^2)$	1.387[e]	1.395	1.357	1.388	1.367	1.357	1.360
$r(N^1–H^{12})$	0.93	1.025	0.956	0.992	–	–	–
$r(C^2–C^4)$	1.439[e]	1.510	1.471	1.485	1.498	1.536	1.518
$r(C^2{=}O^{10})$	1.214[e]	1.205	1.207	1.213	1.236	1.225	1.235
$r(C^4–C^5)$	1.383	1.464	1.391	1.388		1.372	1.381
$r(C^4–C^6)$	1.384[e]	1.403	1.392	1.375		1.370	1.376
$r(C^6–C^8)$	1.391[e]	1.417	1.406	1.394		1.394	1.397
$r(C^8–C^9)$	1.389	1.397	1.402	1.390		1.387	1.390
m.d.[f]	0.0000	0.0204	0.0161	0.0094	0.0000	0.0197	0.0093
$<$ ($H^{12}N^1C^2$)	119	121.4	122.6	123.4	–	–	–
$<$ ($N^1C^2C^4$)	105.6	103.7	104.8	105.1	110.6	108.2	108.9
$<$ ($N^1C^2O^{10}$)	125.1[e]	125.9	125.6	125.8	124.8	129.5	128.6
$<$ ($C^2N^1C^3$)	112.5	117.2	114.9	113.3	107.1	110.9	109.9
$<$ ($C^2C^4C^5$)	108.2	107.6	107.7	108.3		106.3	106.2
$<$ ($C^2C^4C^6$)	130.2[e]	132.9	130.4	130.2		132.1	132.3
$<$ ($C^4C^6C^8$)	116.6	119.8	116.9	117.4		117.7	117.7
$<$ ($C^6C^8C^9$)	121.6	120.7	121.3	121.0		120.6	120.8
m.d.[f]	0.00	2.19	0.79	0.57	0.00	3.63	2.77

[a] For atom numbering see Scheme 2.
[b] Ref. [29].
[c] Ref. [15].
[d] Ref. [30].
[e] Mean values of two non-equivalent positions in the monocrystal.
[f] Mean absolute deviations ($r(N^1–H^{12})$ and $<$ ($H^{12}N^1C^2$) are excluded).

Both the above results for the imides studied can be explained by the conjugation of the nitranionic charge with the carbonyl groups: decrease in C=O bond orders and increase in the C–C ones (Section 4.2), accompanied by an enhancement of the ν_{CO} couplings.

4.2. Energies

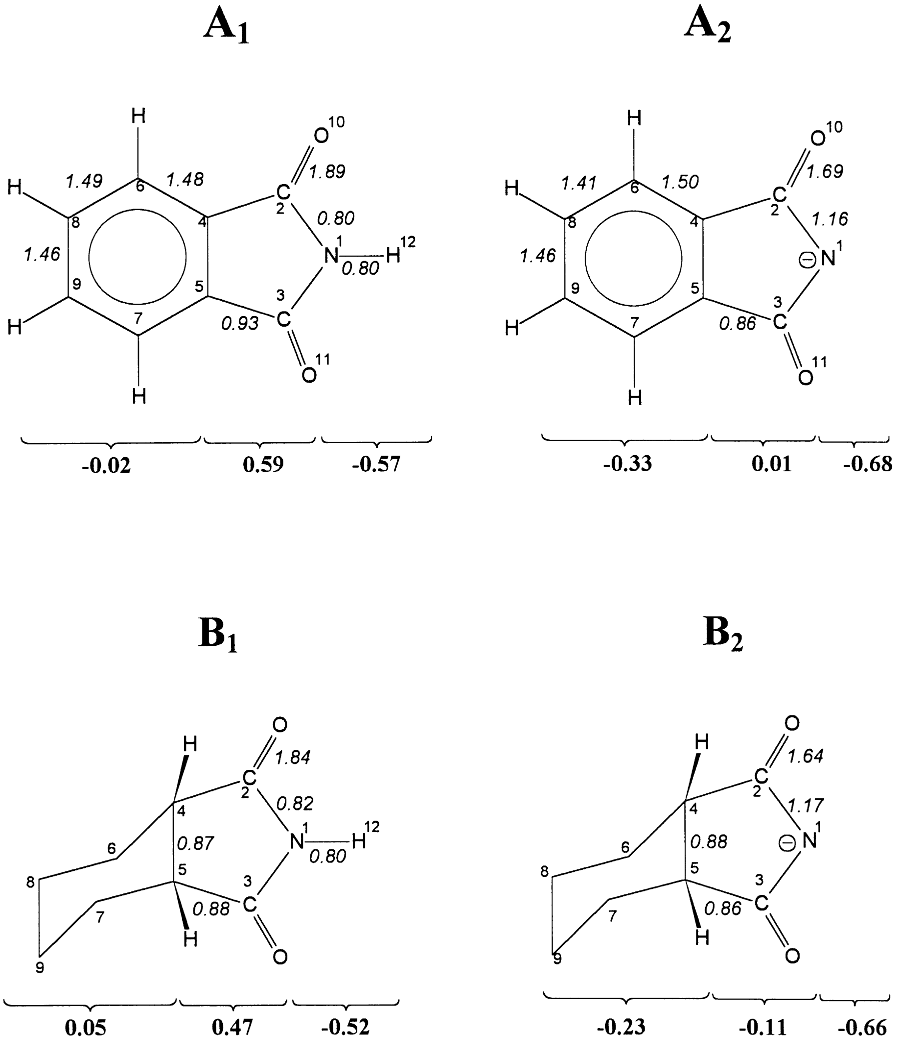
The HF 6-31G total energies of the species studied are, as follows:

$E_{tot} =$ −509.861590h and −509.277209h for the phthalimide molecule and its nitranion, and
$E_{tot} =$ −513.345467h and −512.758965h for *cis*-hexahydrophthalimide molecule and its nitranion, respectively.

The following deprotonation energies $E_D = E_{tot}(\text{nitranion}) - E_{tot}(\text{molecule})$ correspond to the above values:

$E_D =$ 1533.9 kJ mol^{-1} for phthalimide; and
$E_D =$ 1539.5 kJ mol^{-1} for *cis*-hexahydrophthalimide.

We calculated that both *trans*-hexahydrophthalimide molecule and nitranion are less stable (by 14.4 and 20.1 kJ mol^{-1}, respectively) than the corresponding *cis*-isomers, so the corresponding E_D is 1545.2 kJ mol^{-1}. All these values are close to E_D of succinimide, i.e. 1536.3 kJ mol^{-1} [19], and hence correspond to the close acidities of these compounds: pK_as of phthalimide and succinimide are 13.4 and 14.6 (solvent DMSO) [43]. For comparison: E_D of *o*-sulfobenzimide (saccharin) has been calculated to be essentially lower, 1469.5 kJ mol^{-1} (3-21G*) [21] or 1415.7 kJ mol^{-1} (6-31G*) [42], as saccharin is a



Scheme 2. Ab initio RHF/6-31G structure of phthalimide (**A_1**), hexahydrophthalimide (**B_1**) and of their nitranions (**A_2**, **B_2**). The bond orders (in italics) and net electric charges on the fragments (in bold) are indicated in the Formulae.

much stronger acid (pK_a = 4.0) [43] than the above 1,2 dicarboxamides.

4.3. Structure

The structure of the species studied are shown in Scheme 2; the numerical data for their geometry parameters are listed in Tables 5 and 6. At least the following considerations should be mentioned:

1. The 6-31G* geometry parameters correspond best to the X-ray data, however the mean deviations (Table 5) are essentially larger than the experimental errors, which are 0.002–0.005 Å for distances between heavy (non-hydrogen) atoms and 0.2–0.4° for the corresponding angles [29,30], 0.06 Å and 4° for parameters with the participation of hydrogen atoms [29].
2. We have recently found in the case of 2,5-pyrrolidinedione (succinimide) that extensions of the basis set by adding polarization and diffuse functions within the RHF theory results in deterioration in both vibrational and structural parameters.

Table 6
Bond lengths (Å) and bond angles (°) of the hexahydrophthalimide molecule and of its nitranion

Geometry parameters[a]	Molecule		Nitranion	
	3-21G	6-31G	3-21G	6-31G
r(N^1–C^2)	1.384	1.381	1.348	1.354
r (N^1–H^{12})	0.999	0.994	–	–
r (C^2–C^4)	1.522	1.518	1.560	1.544
r (C^2=O^{10})	1.205	1.214	1.229	1.239
r (C^4–C^5)	1.504	1.549	1.528	1.535
r (C^4–C^6)	1.529	1.531	1.529	1.529
r (C^6 C^8)	1.537	1.531	1.537	1.532
r (C^8–C^9)	1.538	1.532	1.539	1.533
$<$ (H^{12}N^{1}C^2)	122.9	122.9	–	–
$<$ (N^{1}C^{2}C^4)	106.0	106.9	110.2	110.9
$<$ (N^{1}C^{2}O^{10})	125.9	125.2	128.9	127.8
$<$ (C^{2}N^{1}C^3)	114.4	114.1	110.9	110.2
$<$ (C^{2}C^{4}C^5)	102.6	103.1	101.1	101.4
$<$ (C^{2}C^{4}C^6)	113.8	115.4	113.0	115.4
$<$ (C^{4}C^{6}C^8)	112.5	113.5	112.5	113.5
$<$ (C^{6}C^{8}C^9)	110.2	110.8	110.3	110.7

[a] For atom numbering see Scheme 2.

3. Nobody could expect complete coincidences between X-ray experimental data for single crystals and theoretical data for isolated molecules or ions.

The essential changes in the C–N and C=O bond lengths (and in the corresponding bond orders, Scheme 2), which accompany the conversion of the phthalimide molecule into the nitranion, have obviously been expected. However, an enlargement in r(C^2–C^4) is almost twice greater than expected (Table 5). There are essential changes in all the pyrrolidine ring angles (Table 5), although it remains planar.

We found no experimental structural data for either hexahydrophthalimide or its nitranion, but on the basis of the above results we assume that calculations (Table 6) will give an adequate description of the structure of these species.

The increase in the P(C–N) bond order by 0.35 units and the decrease in the P(C=O) one by 0.20 units, accompanying the conversion of the 1,2-dicarboximides studied into nitranions, are in a good agreement with the respective changes, both calculated and measured, in the lengths of the same bonds (cf. Scheme 2 and Tables 5 and 6). However, a slight decrease, by 0.07 units only, in P(C^2–C^4) correspond to the strongest bond length change in the phthalimide case, i.e. enlargement: calculated by 0.033 Å, determined experimentally by 0.059 Å (Table 5 and A$_1$, A$_2$ in Scheme 2). In the case of hexahydro-phthalimide case (B$_1$, B$_2$ in Scheme 2) the calculated P(C^2–C^4) decrease is 0.02 units only; the corresponding enlargement of the C^2–C^4 bond is calculated to be 0.026 Å (Table 6).

The net electric charges on the fragments are shown in Scheme 2. They seem to be overestimated, as the dipole moments of 3.92 and 3.17 Debye, calculated for phthalimide and hexahydrophthalimide respectively, are larger than the experimental ones of 2.91 Debye [30] and 2.24 Debye [26] (solvent dioxane). We have recently found that in the case of succinimide both RHF and DEPT theories give quite larger dipole moment values, 2.00–2.86 Debye, than the experimental value of 1.47 Debye [19] and references therein.

The net charge *changes*, $\Delta q = q(\text{nitranion}) - q(\text{molecule})$, resulting from the conversion of the 1,2-dicarboximide molecules studied into the corresponding nitranions, are very informative for showing the distribution of the nitranionic changes. We can calculate on the basis of the data from Scheme 2, that the greater parts of the nitranionic charges, nearly 0.6 e$^-$, are localized within the carbonyl groups, and the rest of them, ca. 0.1 and 0.3 e$^-$, are held by the nitranionic centers and hydrocarbon moieties.

5. Conclusion

As can be seen from this work, conversion of the 1,2-dicarboxamides into the corresponding nitranions results in strong spectral and structural changes. Both these changes can be predicted and described at moderate levels of the ab initio MO theory.

Acknowledgements

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