INTRAMOLECULAR C–H...O HYDROGEN BONDING IN 2-(N-PYRIDINIA)INDANE-1,3-DIONE BETAINES

O. Ya. Neiland, R. B. Kampare,
D. É. Prikule, and É. É. Liepin'sh

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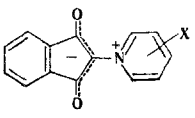
The existence of an intramolecular C–H...O hydrogen bond between the α protons of the pyridinium ring and the oxygen atoms of the phthaloyl part of the molecule in 2-(N-pyridinia)-indane-1,3-dione betaines and their aza analogs was proved by their PMR spectra. This sort of intramolecular hydrogen bond is absent in pyridinium betaines of cyclohexane-1,3-dione and acetoacetic and malonic esters.

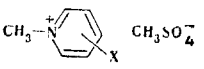
2-(N-Pyridinia)indane-1,3-dione betaines (I) and their analogs (II, III) are generating interest as electron-donor components of charge-transfer complexes (CTC) [1-3]. An x-ray diffraction analysis [4] of the monoclinic modification of crystals of 2-(N-pyridinia)indane-1,3-dione betaine (Ia) unexpectedly showed that its molecule is almost coplanar (the dihedral angle between the planes of the phthaloyl and pyridinium rings does



I a-h

a X=H; b X=3-CH_3; c X=4-CH_3; d X=3-NH_2; e X=4-NH_2; f X=4-CN; g X=3-COOH; h X=4-COOH

TABLE 1. Chemical Shifts of the Protons of Substituted N-Methylpyridinium Methylsulfates



VII

Compound	X	Solvent	δ, ppm			
			H-2, H-6	H-3, H-5	H-4	Remaining signals
Ia	—	$CDCl_3$	9,07	8,08	8,60	4,51 (CH_3N^+); 3,53 (CH_3O)
		d_6-DMSO	9,02	8,14	8,62	4,44 (CH_3N^+); 3,44 (CH_3O)
Ib	3-CH_3	$CDCl_3$	8,97 (H-2); 9,01 (H-6)	7,91	8,25	4,48 (CH_3N^+); 3,62 (CH_3O); 2,58 (CH_3)
		d_6-DMSO	8,83 (H-2); 8,77 (H-6)	7,97	8,38	4,28 (CH_3N^+); 3,39 (CH_3O); 2,47 (CH_3)
Ic	4-CH_3	$CDCl_3$	8,95	7,82	—	4,44 (CH_3N^+); 3,63 (CH_3O); 2,62 (CH_3)
		d_6-DMSO	8,83	7,94	—	4,27 (CH_3N^+); 3,39 (CH_3O); 2,29 (CH_3)
Id	3-NH_2	d_6-DMSO	7,99	7,57	7,57	4,15 (CH_3N^+); 3,40 (CH_3O); 6,50 (NH_2)
Ie	4-NH_2	$CDCl_3$	7,90	6,92	—	3,91 (CH_3N^+); 3,65 (CH_3O)
		d_6-DMSO	8,12	6,83	—	3,84 (CH_3N^+); 3,40 (CH_3O)
If	4-CN	$CDCl_3$	9,42	8,42	—	4,65 (CH_3N^+); 3,67 (CH_3O)
		d_6-DMSO	9,31	8,71	—	4,48 (CH_3N^+); 3,43 (CH_3O)
Ig	3-COOH	$CDCl_3$	9,58 (H-2); 9,31 (H-6)	8,24	8,98	4,57 (CH_3N^+); 3,56 (CH_3O)
		d_6-DMSO	9,50 (H-2); 9,17 (H-6)	8,22	8,95	3,41 (CH_3N^+); 3,37 (CH_3O)
Ih	4-COOH	$CDCl_3$	9,26	8,43	—	4,59 (CH_3N^+); 3,62 (CH_3O)
		d_6-DMSO	9,17	8,46	—	4,49 (CH_3N^+); 3,40 (CH_3O)

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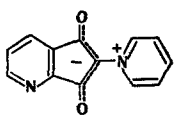
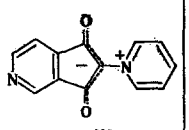
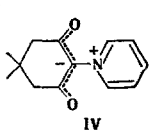
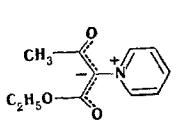
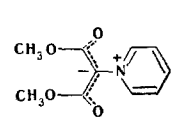
TABLE 2. PMR Spectra of 2-(N-Pyridinia)indane-1,3-dione Betaines Ia-h and Some of Their Analogs (II-VI) and Additive Contributions (ΔH_i) of the Anionic Part of the Molecule to Shielding of the Pyridinium Protons

Compound	Solvent	δ, ppm				$\Delta H_i = \delta_i$ (betaine) − δ_i(N-methylpyridinium)		
		H-2′, H-6′	H-3′, H-5′	H-4′	Remaining protons	H-2′, H-6′	H-3′, H-5′	H-4′
Ia	$CDCl_3$	10,22	7,80	7,80	7,53 (C_6H_4)	1,15	−0,28	−0,80
	d_6-DMSO	9,84	8,10	8,10	7,48 (C_6H_4)	0,82	−0,04	−0,52
Ib	$CDCl_3$	9,97	7,45—7,60	7,45—7,60	7,48 (C_6H_4); 2,50 (CH_3)	1,0 (H-2′); 1,06 (H-6′)	—	—
	d_6-DMSO	9,60	7,96	7,96	7,45 (C_6H_4); 2,48 (CH_3)	0,77 (H-2′); 0,83 (H-6′)	—	—
Ic	$CDCl_3$	9,94	7,75	—	2,57 (CH_3)	0,99	−0,19	—
	d_6-DMSO	9,57	7,82	—	7,46, 7,39 (C_6H_4); 2,51 (CH_3)	0,74	−0,12	—
Id	$CDCl_3$	9,71 (H-2′); 9,54 (H-6′)		7,24	7,66, 7,58 (C_6H_4); 4,99 (NH_2)	—	—	—
	d_6-DMSO	9,10 (H-2′); 8,92 (H-6′)	7,68	7,33	7,50, 7,47 (C_6H_4); 6,50 (NH_2)	1,11 (H-2′); 0,93 (H-6′)	0,11	−0,24
Ie	$CDCl_3$	8,84	6,91	—	7,44 (C_6H_4)	0,94	−0,01	—
	d_6-DMSO	8,48	6,84	—	7,36 (C_6H_4)	0,36	0,01	—
If	$CDCl_3$	10,68	7,86	—	7,70, 7,67 (C_6H_4)	1,26	−0,56	—
	d_6-DMSO	10,13	8,35	—	7,53 (C_6H_4)	0,82	−0,36	—
Ig	$CDCl_3$	10,84 (H-2′); 10,43 (H-6′)	7,90	8,45	7,62, 7,54 (C_6H_4)	1,26 (H-2′); 1,05 (H-6′)	−0,34	−0,53
	d_6-DMSO	10,52 (H-2′); 10,16 (H-6′)	8,17	8,56	7,56 (C_6H_4)	1,02 (H-2′); 0,96 (H-6′)	−0,05	−0,39
Ih	$CDCl_3$	10,43	8,52	—	7,63, 7,53 (C_6H_4)	1,17	0,09	—
	d_6-DMSO	10,11	8,34	—	7,53 (C_6H_4)	0,94	−0,12	—
 II	$CDCl_3$	10,23	8,10—7,80	8,10—7,80	8,72 (C_5H_3N, H-5) 8,10—7,80 (C_5H_3N, H-6, H-7)	1,16	—	—
	d_6-DMSO	9,73	8,16	8,36	8,71, 7,87, 7,01 (C_5H_3N)	0,71	0,02	−0,26
 III	$CDCl_3$	10,22	7,86	8,05	8,89, 8,84, 7,52 (C_5H_3N)	1,15	−0,03	−0,55
	d_6-DMSO	9,73	8,18	8,40	8,92, 8,70, 7,52 (C_5H_3N)	0,71	0,04	−0,44
 IV	$CDCl_3$	8,62	7,72	8,18	2,39 (CH_2); 1,11 (CH_3)	−0,45	−0,36	−0,42
	d_6-DMSO	8,62	7,97	8,40	2,21 (CH_2); 1,04 (CH_3)	−0,40	−0,17	−0,22
 V	$CDCl_3$	8,49	7,75	8,16	4,13 (CH_2O); 2,46 (CH_3); 1,23 (CH_3CH_2)	−0,58	−0,33	−0,44
	d_6-DMSO	8,67	7,97	8,47	3,95 (CH_2O); 2,24 (CH_3); 1,06 (CH_3CH_2)	−0,35	−0,17	−0,15
 VI	$CDCl_3$	8,55	7,80	8,11	3,74 (OCH_3)	−0,52	−0,38	−0,49

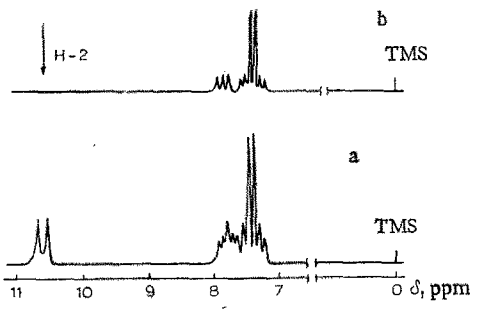


Fig. 1. PMR spectrum of 2-(4'-N-cyanopyridinia)indane-1,3-dione betaine (If): a) total spectrum; b) double-resonance-irradiated pyridinium 2-H protons.

not exceed 3°), while the α-hydrogen atoms (2'-H and 6'-H) of the pyridine ring are in direct proximity to the oxygen atoms (the O...2'-H distance is 2.1, and the O...2'-C distance is 2.87 Å [4]). One may evidently speak of an unusual intramolecular hydrogen bond (IHB) between the 2'-H and 6'-H atoms and the oxygen atom of the anionic system. We therefore studied the PMR spectra of I, their analogs II and III, and derivatives of cyclohexane-1,3-dione (IV), acetoacetic ester (V), and malonic ester (VI) (Table 2). For comparison, we recorded the PMR spectra of a number of N-methylpyridinium methylsulfates (VII) (Table 1).

A considerable paramagnetic shift of the signals is observed for the 2'-H and 6'-H protons of I-III as compared with the corresponding N-methylpyridinium methylsulfate (ΔH_i = 0.94-1.26 ppm in $CDCl_3$ and 0.36-0.94 ppm in d_6-DMSO), but this is not the case for IV-VI. The signals of the other protons of the pyridine ring, on the other hand, experience a certain shift to strong field. This sort of behavior of the 2'-H and 6'-H signals of I-III can be explained by the formation of O...2'-H and O...6'-H IHB; this is due to the sterically favorable orientation of the oxygen atoms of the five-membered indanedione grouping and the 2'-H and 6'-H atoms of the pyridine ring. In the case of a six-membered ring (IV) the large valence angle of 120° of the $C^1C^2C^3$ bonds draws together the oxygen and 2'-H and 6'-H atoms so strongly that the forces of repulsion are operative, and the pyridine ring is turned away from the $OC^1C^2C^3O$ plane, as a consequence of which an IHB is not formed. It may be supposed that similar reasons are responsible for the pronounced noncoplanarity of the molecules of V and VI, in which an IHB is not observed.

Electron-acceptor substituents in I lead to an increase in the ΔH_i values, whereas electron-donor substituents, on the other hand, lead to a decrease in these values; this is apparently expalined by a change in the polarity of the C–2'-H bond and consequently to an increase (or decrease) in the energy of the IHB. A correlation between the σ_n values of the substituents and the ΔH_i values for the 2'-H and 6'-H atoms is observed here:

$$\Delta H_i = 0.26\sigma_n + 1.10 \quad (r = 0.95,\ s = 0.04).$$

The observed weak-field shifts of the 2'-H and 6'-H protons of I-III are smaller in d_6-DMSO than in $CDCl_3$ (Table 2); this may be associated with specific solvation leading to a decrease in the energy of the IHB.

A long-range constant ($^3J_{N-C-C-H}{}^{14}$ = 3 Hz) of coupling with the 3'-H and 5'-H protons is observed for If (Fig. 1). However, the electron-density distribution about the nitrogen atom in pyridinium salts [5] is usually the reason for the strong quadrupole relaxation, as a consequence of which it is impossible to observe the constants of spin–spin coupling of the ring protons with the nitrogen atom at room temperature.

EXPERIMENTAL

The PMR spectra of $1 \cdot 10^{-1}$ mole/liter solutions of the compounds were recorded with a Perkin–Elmer R-12A spectrometer (60 MHz) with tetramethylsilane as the internal standard.

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