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Peri Interaction in Naphthalene Ketones

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Peri interaction in several naphthalene ketones was investigated using the carbon-13 NMR, IR, and UV spectra. The carbonyl carbon resonances for 7*H*,14*H*-cycloocta[1,2,3-*de*:5,6,7-*d'e'*]dinaphthalene-7,14-dione and its 7-oxa analog were found to be shifted upfield by 27 and 24 ppm respectively compared with those of model compounds. The anomalous shift for the former was attributed to π-orbital compression, which inhibited the polarization of carbonyl groups because of a forced parallel geometry, while the latter was attributed to field effects. The conclusion was supported by UV and IR data.

Recently we have observed the unusual chemical shifts for the sterically perturbed sp^2 carbon resonances in certain cyclophanes.[1] Unlike the conventional steric effects on the carbon chemical shifts,[2] which in general lead a resonance upfield through the charge polarization of the C–H bonds induced by the steric compression, this new type of steric effect seems to be caused by the interactions between π-orbitals along the orbital axis. In order to distinguish these two sterically induced shifts with opposite signs, we call the former (conventional) shifts "σ-orbital compression shifts" and the latter (new), "π-orbital compression shifts."

As the π-compression shifts may conveniently be used to assess the steric perturbation of π-orbitals, we have studied the proximity effects on the carbonyl carbon chemical shifts of naphthalene peri ketones, whose peri positions are only 2.4—2.5 Å apart.[3] The structural features of these ketones were also investigated in order to obtain collaborative evidence of the π-orbital compression effect.

Experimental

Spectral Measurements. The carbon-13 NMR spectra were recorded using a JEOL JNM FX-60 spectrometer equipped with a JFA-100 data system (8 K) operating at 15.00 MHz. The sample was dissolved in $CDCl_3$. The concentration was *ca.* 0.2 M except for **3**, for which a saturated solution was used. The samples were contained in 10 mm o.d. tubes. The spectra were obtained by storing the free induction decays produced by a series of 9 μs r.f. pulses (45° pulse), followed by the Fourier transformation. The sample temperature was 25 °C. Generally, 4 K data points (real 2 K points) were collected for a sweepwidth of 4 kHz, giving an effective resolution of 2 Hz (±0.13 ppm). The delay between pulses was 3—5 s, and 500—1000 transients were required to obtain a good signal-to-noise ratio. The chemical shifts are shown in a δ value downfield from the internal TMS.

The carbonyl stretching frequencies in the IR spectra were recorded using a Perkin-Elmer 225 spectrometer on samples dissolved in $CHCl_3$ (0.25 and 0.5% solutions) using a 1-mm cell. A symmetrical carbonyl band was observed in the expanded spectrum (×8) except for **4a**, which showed low-intensity bands at 1632 and 1623 cm^{-1} in addition to a strong band at 1653 cm^{-1}. The data are collected in Table 1, together with the shift and frequency differences from **1**.

The UV spectra were recorded on a Hitachi-124 spectrometer, using 95% ethanol as the solvent. The data are summarized in Table 3, while some representative curves are shown in Fig. 1.

*7-Oxa-7*H*,14*H*-cycloocta[1,2,3-*de* : 5,6,7-*d'e'*]dinaphthalene-14-one (**4a**).* A mixture of 6.3 g (0.02 mol) of 8-(1-naphthyloxy)naphthalene-1-carboxylic acid (mp 128.5—130 °C), prepared by the Ullmann reaction between ethyl 8-bromonaphthalene-1-carboxylate[4] and sodium 1-naphthoate in DMF, using cupric oxide as the condensing reagent, followed by hydrolysis, and 300 g of polyphosphoric acid was warmed at 100 °C for 30 min. A usual work-up subsequently gave pale yellow needles; mp 210—212 °C; recrystallized from benzene; *m/e* 296; δ (C), 118.7, 123.4, 124.4, 124.9, 126.0, 127.0, 128.0, 128.6, 129.6, 130.4, 131.9, 133.2, 134.0, 134.5, 135.8, 136.9, and 173.2. Found: C, 84.31; H, 4.07%. Calcd for $C_{21}H_{12}O$: C, 85.12; H, 4.08%.

*7-Thia-7*H*,14*H*-cycloocta[1,2,3-*de* : 5,6,7-*d'e'*]dinaphthalene-14-one (**4b**).* A mixture of 2.1 g (6.4 mmol) of 8-(1-naphthylthio)naphthalene-1-carboxylic acid (mp 202—203.5 °C), prepared by the Ullmann reaction between ethyl 8-bromonaphthalene-10-carboxylate and sodium 1-naphthalenethiolate, followed by hydrolysis, and 77 g of polyphosphoric acid was heated at 120 °C for 7.5 h after the literature method.[6] Pale yellow needles; mp 235.5—236.5 °C; recrystallized from benzene; *m/e* 312; δ (C), 123.1, 126.0, 127.3, 128.3, 129.9, 130.9, 133.2, 134.5, 137.7, 146.2, 200.5. Found: C, 80.69; H, 3.81%. Calcd for $C_{21}H_{12}S$: C, 80.74; H, 3.87%.

*12*H*-Benzo[*f*]naphtho[1,8-*bc*]oxepin-12-one (**5c**).* The acyl chloride obtained from 8-phenoxy-1-naphthoic acid (21.5 g, 0.082 mol) was dissolved in 100 ml of benzene, and to this we added 22 g (0.10 mol) of aluminum chloride. Column chromatography on silica gel gave pale yellow needles; mp 97.5—98.5 °C; 10% yield. Found: C, 83.33; H, 4.05%. Calcd for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09%.

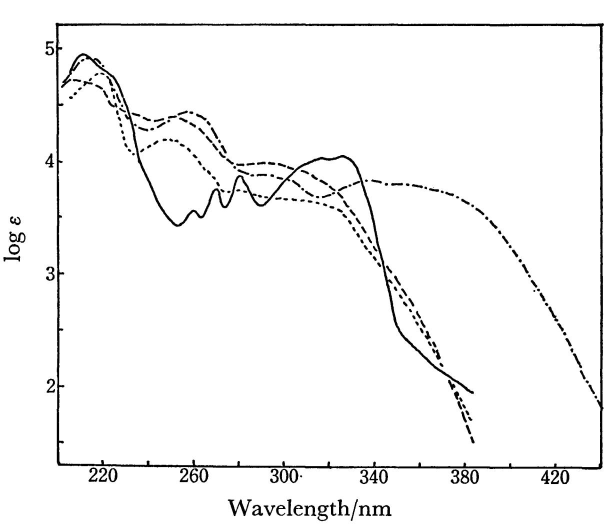
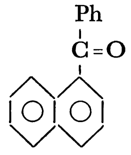
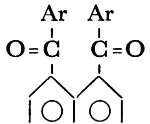
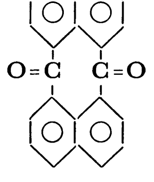
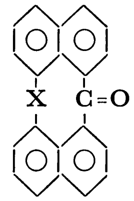
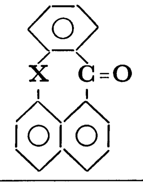


Fig. 1. UV spectra in 95% ethanol; —— **3**, ······ **1**, ---- **2**, and -·-·- **4a**.

Table 1. Carbon-13 NMR and IR data

Compound			Carboon-13 NMR, δ/ppm		IR, ν/cm^{-1}	
			C=O	$\Delta\delta$$^{a)}$	$\nu_{C=O}$	$\Delta\nu_{C=O}$$^{b)}$
	**1**		197.6	—	1660	—
		Ar				
	2a	Ph	197.6	0	1660	0
	2b	*p*-tolyl	197.3	−0.3	1656	−4
	2c	1-naphthyl	198.4	+0.8	1660	0
	**3**		170.9	−26.7	1685	+25
		X				
	4a	O	173.2	−24.4	1653	−7
	4b	S	200.5	+2.9	1662	+2
		X				
	5a	CH_2	198.9	+1.3	1654	−6
	5b	CO	196.0	−1.6	1658	−2
	5c	O	193.8	−3.8	1659	−1

a) Chemical-shift differences for carbonyl carbons with respect to the shift for **1**. b) Difference in carbonyl stretching frequencies compared with **1**.

Table 2. Carbon-13 NMR chemical shifts, $\delta^{a)}$

Compound	Chemical shift, δ/ppm		
	C=O	Ar–C	CH_3
1	197.6	*136.2*, *133.6*, *132.4*, 133.0, 131.0, 130.3(×2), 128.3(×2), 127.7 127.1, 126.4, 125.6, 124.1	
2a	197.6	*137.7*, *137.1*, *135*.1, *132.7*, 131.9, 130.4(×2), 128.8, 128.0, 124.9	
2b	197.3	*143.5*, *137.3*, *135.1*, 131.7, 130.6(×2), 129.6, 128.8(×2), 124.8	21.7
2c	198.4	*153.2*, *141.9*, *135.6*, *134.9*, 133.6(×2), 132.5, 131.5, 129.2, 127.9, 127.4(×2), 125.2, 124.1	
3	170.9	129.9, *128.4*, 126.1, *125.2*, 124.4, *120.4*	
5c	196.0	*138.3*, *136.2*, 135.1, *133.8*, 132.8, 132.2, 127.8, 126.0	

a) Numbers in italic denote non-protonated carbons. Resonances due to the doubly overlapped carbons are shown by 2 in parentheses.

Results and Discussion

The naphthalene peri ketones examined in this paper, **1**—**5**, are shown in Table 1. 1-Benzoyl- (**1**)[5] and 1,8-diaroyl-naphthalenes (**2**),[6] 7*H*,14*H*-cycloocta[1,2,3-*de*: 5,6,7-*d′e′*]dinaphthalene-7,14-dione (**3**),[7] 7(12*H*)-pleiadenone (**5a**),[8] and 7,12-pleiadenedione (**5b**)[8] were prepared according to the reported method. 7-Oxa-7*H*,14*H*-cycloocta[1,2,3-*de* : 5,6,7-*d′e′*]dinaphthalene-14-one (**4a**) and sulfur analog **4b**,[9] and 12*H*-benzo[*f*]naphtho[1,8-*bd*]oxepin-12-one (**5c**) were prepared from ethyl 8-bromonaphthalene-1-carboxylate (see Experimental section).

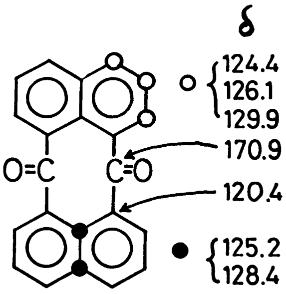
The chemical shift of the carbonyl-carbon resonances for these compounds are shown in Table 1, in which are also shown the chemical-shift differences, Δδ's, from that of the reference compound **1**. The carbon-

Table 3. UV spectra data in 95% ethanol

Compound	λ_{max}/nm (log ε)
1	220(4.79), 250(4.20), 280 sh(3.75), 290 sh(3.69), 306(3.67), 320 sh(3.60)
2a	206(4.72), 230 sh(4.40), 250(4.40), 290(3.99), 310 sh(3.91)
2c	216(5.02), 230 sh(4.79), 250 sh(4.35), 316(4.28)
3	212(4.95), 226(4.73), 250 sh(3.49), 259(3.56), 269(3.77), 280(3.87), 3.16(4.03), 326(4.05)
4a	215(4.89), 257(4.42), 293(3.87), 303 sh(3.82), 333(3.81), 356 sh(3.76)
4b	214(4.89), 253 sh(4.28), 258 sh(4.27), 270 sh(4.09), 293(4.01), 308(3.98), 333(3.84)
5a	210(4.63), 245(4.26), 336(3.92)
5b	206(4.66), 240(4.47), 280 sh(3.62), 335(3.39)

13 NMR data for selected compounds are summarised in Table 2. Quaternary carbon resonances were assigned by means of the ^{1}H single-frequency off-resonance decoupling (SFORD) technique. The protonated aryl carbon resonances having double intensity are designated in Table 2. The carbon-13 NMR spectra for the less symmetrical **4a**, **4b**, **5a**, and **5b** were too complex to analyze. The data for these compounds are, therefore, not included in Table 2.

Taking compound **3** as an example, the procedures of the assignment will now be illustrated. Compound **3** showed a carbonyl resonance at δ 170.9, together with six aromatic carbon resonances. The aromatic carbon peaks at δ 120.4, 125.2, and 128.4 were attributed to the protonated carbons by means of the SFORD technique. The lowest field resonance, at δ 120.4, was assigned to the carbon directly bonded to the carbonyl group, since it appeared as the double intensity peak. The resonances at δ 124.4, 126.1, and 129.9 all appeared as double-intensity peaks which were split into doublets in the SFORD spectrum.



The chemical shifts of the carbonyl carbons depend strongly upon the conjugative interactions between the adjacent unsaturated bonds. The chemical shifts of the carbonyl carbons in the conjugated systems usually appear at a higher field than those in the non-conjugated systems. For example, the carbonyl carbon for di-*t*-butyl ketone at δ 215.8 is shifted to δ 195.2 for benzophenone.[10)]

Carbonyl-carbon resonances for **1**, **2a**, **2b**, and **2c** at δ 197—198 are only slightly downfield from those of the unhindered aryl ketone ($\Delta\delta$ *ca.* 3 ppm). These slight downfield shifts may result from the peri interactions, which might inhibit the conjugation between the naphthalene ring and the carbonyl group. Because of additional conjugation in the benzoyl moiety, the extent of conjugation inhibition by the peri interaction in these systems could not be correctly estimated. The situation, however, may not be as serious as in the case of 9-acetylanthracene ($\Delta\delta$ 11 ppm),[10)] in which two peri interactions exist. The UV spectral data for **1** and **2** in Table 3 revealed that the conjugations between the naphthalene ring and carbonyl groups were quite similar to each other, as is shown in Fig. 1.

With the 8-membered cyclic compound **3**, the carbonyl carbon resonance appeared at δ 170.9, which is, to our best knowledge, the highest field signal thus far reported for ketones. The shift difference, $\Delta\delta$, from compound **1** was -26.7 ppm. This observation is somewhat surprising, since the compound has a rigid structure in which two carbonyl groups are parallel to each other and are nearly perpendicular to the naphthalene ring plane.[11)] The UV spectrum of **3** shows that the naphthalene chromophores are in an unfavorable geometry for conjugation (Table 2, Fig. 1). Furthermore, the 8-membered ketones have been known to show the $\delta_{C=O}$ at the lowest field among the other cycloalkanones.[12)] Both the electronic and ring-size considerations call for downfield shifts of carbonyl carbons, the opposite of what we have observed. It is, therefore, apparent that a possible angle strain can not be responsible for the observed anomalous chemical shift.

Instead, we attribute the primary origin of the unusual up-field shift to the increased double-bond character of the carbonyl group in **3**, possibly caused by the inhibition of the carbonyl-bond polarization. In this compound, not only do two carbonyl groups come into a parallel geometry, but also the π electrons interact directly by means of the forced paralled orientation. The latter situation can not be expected for the related *s-cis* α-diketone, in which the nordal planes of the carbonyl carbons lie nearly on a single plane.

Carbon-13 upfield shifts were observed for all the other naphthalene carbon resonances in **3**, indicating the increased electron density of the aryl carbons in **3**. Especially, the resonance due to the carbons directly bonded to the carbonyl group was shifted upfield by more than 10 ppm from the equivalent resonances for 1 and 2. This may indicate a partial inhibition of the conjugation between carbonyls and aryl rings, which in turn increases the electron density of the aryl rings in **3** relative to those in **1** and **2**.

The carbonyl-stretching frequency of **3** was shifted by 25 cm^{-1} to 1685 cm^{-1} compared to that of the model compound **1**, indicating the increased double-bond character of the carbonyl group, again caused by the conjugation inhibition. Part of this frequency shift should also be ascribed to the $\angle$C–CO–C deformation characteristic of the medium-sized cyclic ketones, which also show $\nu_{C=O}$ at a high frequency. The IR as well as UV spectral data are consistent with our interpretation of the anomalous chemical shift of the carbonyl carbons for **3**.

In order to obtain further insight into the stereochemical features of **3**, we have examined two analogs, **4a** and **4b**, in which one of the carbonyl groups in **3** is replaced by oxygen or by sulfur respectively. The carbonyl carbon in **4a** was observed at δ 173.3, at a field higher by 24.4 than that of **2a**. Unlike **3**, however, $\delta_{C=O}$ of **4a** appeared at a frequency lower by -7 cm^{-1} than that of **1**. Nakashima and Maciel[14] observed the $\nu_{C=O}$ in 4-oxacyclooctanone shifted by 3.9 ppm compared to cyclooctanone and attributed the phenomenon to the electric-field effect. As the nitrogen analog showed an upfield shift of 13 ppm, they considered this upfield shift to be caused by the transannular effect arising from the through-space charge-neutralization proposed by Leonard *et al.*[15] The upfield shift for **4a** may also be due to the transannular effects. The **4b**, sulfur analog, gave a less anomalous chemical shift for the carbonyl carbon, perhaps because of the enlarged ring size and also the poor electron-donating ability of sulfur compared to oxygen. Because of the substantial geometrical difference, no further comparison between acyclic models and **4** was attempted.

The **4a**, oxygen analog, showed a high intensity plateau at a long wavelength, indicative of substantial conjugation. The sulfur analog **4b** also exhibited an UV absorption similar to that of **4a** but the long wave band fell off to a shorter wavelength. The conformational rigidity of an 8-membered ring in **4b** was confirmed by Johnson *et al.*[6] using a derivative of **4b**.

The pleiadene ketones, **5a**, **5b**, and **5c**, are less anomalous with respect to the carbon-13 NMR and IR data. That these have conformational mobility and undergo inversion at an appreciable rate is shown by the variable temperature NMR spectra.[16] Two carbonyl groups are not in a parallel geometry, but point outward in **5b**. Conjugation between carbonyl and aryl groups dominates these compounds, as is shown by the data in Tables 1 and 3.

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