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PREPARATIONS AND PROPERTIES OF PSEUDO-GEMINAL KETONES OF TRIS-[2.2.2]- AND TETRAKIS[2.2.2.2]PARAZYLYLENE

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Abstract—Pseudo-geminal bridged ketones of tris[2.2.2]paraxylylene, **1**, and of tetrakis[2.2.2.2]paraxylylene, **2**, were prepared and their spectral properties were investigated in comparison with those of dibenzosuberone, **3**. The CO stretching band of **1** was observed at abnormally high frequency region (by *ca.* 50 cm^{-1}) compared with that of **3**, while that of **2** was at a position similar to that of **3**. The electronic spectrum of **1** showed that **1** has enormous loss of conjugation due to lack of coplanarity between CO and aromatics. The chemical shift of H^{0}, *ortho* to CO, of **1** also supported this structural characteristic.

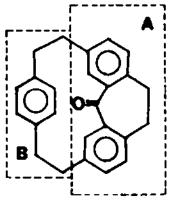
Although two aromatic rings of lower paraxylylenes lie close, little attempt has been made to link these two aromatic rings with one more carbon bridge probably because of difficulties associated with their preparations due to the rigidity of the parent hydrocarbons (e.g. [2.2]paracyclophane). The authors have found that carboxytris[2.2.2]- or carboxytetrakis [2.2.2.2]-paraxylylene underwent quite easily an intramolecular cyclization reaction, giving the corresponding cyclized product, respectively, i.e. the corresponding ketone linked at pseudo-geminal position, in excellent yield.

In a Dreiding model, the pseudo-geminal ketone thus prepared from tris[2.2.2]paraxylylene, **1**, is expected to have a CO group nearly perpendicular to the adjacent benzene planes and to have aromatic moieties A and B (in 1) in close proximity.

In this paper, the preparations and some interesting spectral properties of **1** and the pseudo-geminal ketone of tetrakis[2.2.2.2]-paraxylylene, **2**, are described.

Preparations. **1** was prepared by the intramolecular cyclization reaction of carboxytris[2.2.2]paraxylylene[1] and was obtained as colorless prisms, m.p. 215·0–215·5°, in 84% yield. Similarly **2** was prepared from carboxytetrakis[2.2.2.2]paraxylylene,[2] as slightly pale yellow prisms, m.p. 195–203°,[a] in 93% yield.

IR. Spectra. Carbonyl stretching, ν_{C-O}, is one of the most sensitive vibrations to structural change.[3] The ν_{C-O} values of **1**, **2** and dibenzosuberone,[4] **3**, measured in carbon tetrachloride are shown in Table 1. An abnormally large high-frequency shift (*ca.* 50cm^{-1}) of ν_{C-O} was observed for **1** compared with the reference compound, **3**, while ν_{C-O} of **2** showed only a slight migration (*ca.* 7 cm^{-1} upward). The high frequency shift of ν_{C-O} observed for some of the formally conjugated aryl or diaryl ketone is mainly ascribed to loss of conjugation due to lack of coplanarity between CO and aromatic moieties in a sterically hindered situation.[3] However, aromatic ketones which seem to have normal internal C–C–C bond angles and to have little or poor conjugation were reported to have unexpectedly small high-frequency shifts. Thus only a +9 cm^{-1} shift was observed for the ν_{C-O} value of acetomesitylene compared with that of acetophenone,[3] or an 18 cm^{-1} difference was reported for the ν_{C-O} value of 1-keto[2.2]paracylophane relative to that of *p*-methyl acetophenone.[6,b] Therefore in our present ketones, some



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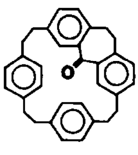

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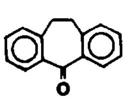

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Table 1. Carbonyl stretching band (ν_{C-O}) of the ketones[a]

	ν_{C-O} (cm^{-1})	
1	1701 sh[b]	1698
2	1664 sh	1656
3	1654	1649

[a] Hitachi EPI-G3 grating infrared spectrophotometer, *ca* 10^{-2}M solution of carbon tetrachloide.

[b] Shoulder.

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[a] Namely, 2 seemed to change its crystal structure from prisms and melted completely at 203°.

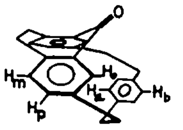
[b] A statistical correction for the ν_{C-O} values because of a rotation about the C–C single bond was not considered. Probably this rotation should be one of the reasons which do not expand the difference of the ν_{C-O} values remarkably. For example, more sterically hindered aromatic ketone such as 2,4,6 - tri - *t* - butyl - acetophenone was reported to show ν_{C-O} at about 1700 cm^{-1} (by *ca.* 10 cm^{-1} high-frequency) than acetomesitylene in carbon tetrachloride.[5]

additional effects which cause high-frequency shift should be operative as well as loss of conjugation. One possibility is an angle strain at a small internal C–C–C bond angle which brings about the ν_{C-O} toward high frequency effectively as seen in a series of alkanones.[7] Halford has given a formula for the ν_{C-O} values of aliphatic ketones as a function of the internal bond angle ψ

$$\nu_{C-O}(\mathrm{cm}^{-1}) = 1278 + 68\,k - 2{\cdot}2\,\psi\ (\text{degrees})$$

where k was the CO stretching force constant for an aliphatic ketone. It was shown that k was equal to $(10{\cdot}2 \pm 0{\cdot}3) \times 10^{-5}$ dynes/cm and was almost independent of the internal bond angle ψ.[7] Schleyer and Nicholas used this equation for evaluation of internal bond angles of cyclic alkanones with slight modification (i.e. k = 10·244 instead of k = 10·2).[8] Using the Schleyer's equation and the estimated difference (8·5°) between the internal bond angle of 1 and of 3 based on Dreiding models, the high-frequency shift due to angle strain is calculated to be 19 cm^{-1} which is still too small to account for the large observed high-frequency shift.[c] Consequently we conclude that both effects, loss of conjugation and bond angle strain, must be responsible for the high-frequency shift observed for 1 because of the rigidity of its structure, though their relative magnitudes are not clear at present.

PMR spectra. Observed chemical shifts and spin-spin coupling constants of **1**–**3** are listed in Table 2, and especially aromatic regions of the spectra of **1** and **2** are shown in Fig. 1. Assignments of aromatic protons were made on the spin decoupling experiments. Since two protons, H^a's, of **1** locate just above (3·0 Å) the "face"[d] benzene ring (A) in a Dreiding model, protons at 4·49 τ were assigned as H^a's. This absorption is considerably shifted to high field (by 1·09 ppm) compared with the aromatic protons of the parent tris[2.2.2]paraxylene (sharp singlet at 3·40 τ),[1] and is similar to aromatic protons observed at 4·50 τ, which locate just above (3·1 Å) aromatic rings of 4,5,7,8-dibenzo[2.2]-paracyclophane.[11] While H^a and H^b of **1** had no ortho coupling, those of **2** showed a normal ortho coupling (by 8·5 Hz). Thus relative positions of H^a and H^b of **2** should be ortho to each other, but it can not be determined which protons should be assigned as the higher or the lower ones.



The chemical shifts of H^o, ortho proton to carbonyl, of **1** and **2**, appear (a) in higher field than that of H^m (by 0·79 ppm for **1**) or H^p (by 0·95 ppm for **1** and by 0·18 ppm for

Table 2. Proton magnetic resonance spectra of the ketones[a]

	H^o	H^m	H^p	H^a	H^b	CH_2	
1	3·79 d	3·00 q	2·84 d.q	4·49 m	2·97 m	6·6 ~ 7·8 m	$J(H^m - H^p) = 8{\cdot}0$ Hz
							$J(H^o - H^p) = 2{\cdot}0$ Hz
2	2·92 d	2·92 q	2·74 d.q	3·07 m.q		6·92 br.s	$J(H^m - H^p) = 7{\cdot}5$ Hz
				3·20 m.q		7·04 br.s	$J(H^o - H^p) = 2{\cdot}0$ Hz
						7·06 br.s	$J(H^a - H^b) = 8{\cdot}5$ Hz
3	2·0 m	2·6 ~ 2·9 m				6·90 br.s	

[a] Varian HA-100 nmr spectrophotometer, with 1% tetramethylsilane as an internal standard, *ca.* 5% in deuteriochloroform, chemical shifts in τ values at 31°. Abbreviations are: br.s, broad singlet; d, doublet; q, AB quartet; d.q, doublet of AB quartet; m.q, multiplet of AB quartet; m, multiplet.

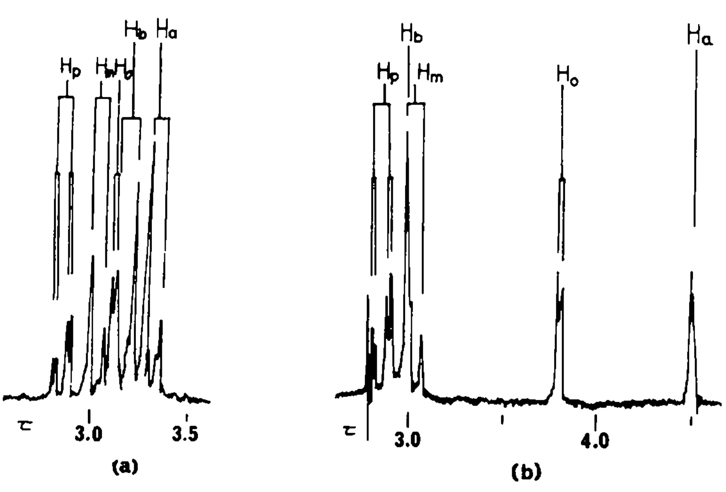


Fig. 1. The aromatic regions of the PMR spectra of the ketones. a, 2; b, 1. As for notations of protons, refer Table 2.

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[c] From recent studies on some cycloalkanones,[9] it seems that such a simple linear relation among the ν_{C-O} values and the internal C–C–C bond angles is not existed exactly.

[d] Terminology of "face" and "lateral" were used for janusene by Cristol.[10] The authors wish to use these terminology to distinguish two limiting conformations of aromatic rings of higher paraxylylenes.

2), and (b) in surprisingly higher field than that of H^o of **3** (by *ca.* 1·8 ppm for **1** and by *ca.* 0·9 ppm for **2**). In contrast to the observation (a), H^o of **3** or ortho protons of simple carbonyl derivatives of tris[2.2.2]- or tetrakis[2.2.2.2]-paraxylylene such as acetyltris[2.2.2]paraxylylene were observed at lower field (by 0·5–1·2 ppm)[1,2] than H^m or H^p. Therefore these high τ values of H^o's of **1** or **2** are attributable (a) mainly to the shielding effect of the "face" benzene ring, (b) particularly for **1** to elimination or considerable reduction of the anisotropic deshielding effect of carbonyl[12] because of nonplanarity between carbonyl and aromatic rings discussed in the IR spectra,[e] and (c) slightly to the inductive effect of the meta substituted methylene bridges. Assuming a conformational similarity between **3** and the A moiety of **1**, the effect due to (a) was approximately evaluated by use of the Johnson-Bovey's method[13] to be *ca* 1·0 ppm upfield for H^o of **1** compared with H^o of **3**. At most 0·3 ppm upfield shift might be responsible for the effect due to (c).[f] Thus this simple calculation suggests that the upfield shift attributed to (b) amounts *ca.* 0·5 ppm.[g] An extra effect to cause the high τ values of H^o, one might consider the deformation of the benzene rings. This seems, however, not to be important, since even [6]paracyclophane which has an apparently very deformed benzene ring, has its aromatic protons at τ 2·83,[15] i.e. in the normal aromatic region. That H^m and H^p of **1** and **2** also appear in the normal aromatic region (τ 2·74 ~ 3·00) affords additional support for the negligible contribution of benzene deformation to the upfield shift of the H^o. More experiments to gain further insights into these effects are being undertaken.

Electronic spectra. The electronic spectra of **1**–**3** measured in methylene chloride, cyclohexane and ethanol are shown in Table 3. According to the low temperature absorption, phosphorescence and degree of polarization spectra of **3**,[16] an absorption at 270 nm is assigned as intramolecular charge-transfer (CT) transition between carbonyl and aromatics, that near 300 nm as the Lb band, and that at 344 nm as the $n\pi^*$ transition in carbonyl. These assignments seem to be valid to the spectra of **1** and **2** considering the wave length and the intensity of the absorptions together with the solvent effects, i.e. the bathochromic shift was observed for the CT and the Lb band and hypsochromic shift for the $n\pi^*$ band in ethanol or methylene chloride solution, though the Lb band of **1** was not clearly observed.

A large hypochromic effect in the CT band and a remarkable hypsochromic shift (21 nm in cyclohexane) of the $n\pi^*$ band are observed for **1** compared with **3**. These characteristics in the electronic spectra are probably connected with the lack of coplanarity of "conjugated" carbonyl[6,17] mentioned above, and indicate again that deformation of the benzene rings is not important, since remarkable bathochromic shifts have often been observed for electronic spectra of cyclophanes containing deformed benzene rings such as [n]paracyclophanes.[15,18]

Table 3. Electronic spectra of the ketones[a]

solvent ketones	methylene chloride λ (nm)	 ε (1/mol . cm)	cyclohexane λ (nm)	ethanol λ (nm)
1	276	4380	271	275
	281 sh[b]	4240		280 sh
	322 sh	280	330	
2	271 sh	11600	268	271 sh
	275	11700		275
	303 sh	4090	295	303 sh
	348 sh	520	351	
3	270	12900	266	270
	296 sh	3740	293 sh	
	344	410	351	342 sh

[a] Hitachi EPS-3T recording spectrophotometer.
[b] Shoulder.

Both the wave length and the intensity of λ_{max} of **2** are very similar to those of **3**, though a slight bathochromic shift due to meta methylene bridges is observed for the CT and the Lb bands of **2**. Thus, similarity between structural environment of a carbonyl in **2** and **3** is again indicated in the electronic spectra, in accord with the IR spectra.

EXPERIMENTAL

All m.ps are uncorrected. Commercially available spectrograde carbon tetrachloride, methylene chloride, cyclohexane, ethanol and deuteriochloroform were used directly for the spectral measurements. The instruments employed for the physical measurements are referred to in the footnotes of the appropriate tables. Mass spectra were taken on a Hitachi RMU-6C spectrometer at 70 eV.

Starting materials for preparations of the ketones. From *p*-xylylene chlroide were prepared tris[2.2.2]paraxylylene (3°-PX) and tetrakis[2.2.2.2]paraxylylene (4°-PX) by the modified Wurtz reaction using sodium-tetraphenylethylene complex, separated through a silica gel column and purified by recrystallization from n-hexane or a n-hexane-benzene mixture. Acetylation of 3°-PX was by use of acetylchloride instead of Ac_2O[1] at −70° in methylene chloride, so the procedure was described in detail. Then, carboxytris[2.2.2]paraxylyene was prepared by the bromoform reaction of acetyltris[2.2.2]paraxylylene,[1] separated through a silica gel column and used without further purification. Carboxytetrakis[2.2.2.2]paraxylylene was prepared by the same methods as described[2] from 4°-PX.

Acetyltris[2.2.2]*paraxylylene.* To a stirred mixture of 2·2 g (29 mmole) of acetyl chloride, 4·9 g (39 mmole) of $AlCl_3$ and 50 ml methylene chloride at −70°, a soln of 6·0 g (19 mmole) of 3°-PX in 100 ml methylene chloride was added dropwise for 1·5 hr keeping the temp. at −70°. After additional stirring for 2 hr at −70°, the mixture was poured into the mixture of ice and HCl, and extracted with methylene chloride. The extract was washed with sat. NaCl aq, with $NaHCO_3$ aq and then with sat. NaCl aq. The soln was dried over Na_2SO_4 and the solvent was evaporated. The residue was chromatographed on a silica gel column. First elution with light petroleum gave 2·4 g (40%) of the recovered 3°-PX and further elution with light petroleum-methylene chloride (1 : 1) gave 3·9 g (52%) of acetyltris[2.2.2]paraxylylene (96% based on 3°-PX consumed). This acetyl derivative was used directly for the bromoform reaction without further purification.

***Pseudo-geminal ketone of tris*[2.2.2]*paraxylylene* (1).** To a soln of 744 mg (2·1 mmol) carboxytris[2.2.2]paraxylylene in 40 ml $POCl_3$ were added 4 g of freshly powdered $ZnCl_2$. The mixture was stirred at 60° until the yellow color of the soln change to orange (1 hr). Then the mixture was poured onto ice with care stirring and extracted with ether-benzene (1 : 1). The ether-

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[e] Preliminary PMR measurement for pseudo-geminal methanotris[2.2.2]paraxylylene, **4**, prepared by the reduction of **1** and dibenzosuberane, **5**, showed no remarkable change of the chemical shift difference between H^m or H^p of **1** and that of **4**, (−0·12 or −0·28 ppm, respectively) compared with the corresponding protons of **3** and those of **5**, (−0·2 ppm).

[f] 2-Proton of 3-methylbenzaldehyde absorbed at higher field by 0·24 ppm than that of benzaldehyde.[14]

[g] Aromatic protons of a conjugated benzene ring of 1-keto[2.2]paracyclophane was reported to absorb as a singlet at τ 3·37[6] i.e., by 1·28 ppm higher field than H^o's of acetophenone (τ 2·09).[14] According to our present discussion, the upfield shift attributed to (b) for this ketone was estimated to be *ca* 0·3 ppm ($0{\cdot}3 \approx 3{\cdot}37 - 2{\cdot}09 - 0{\cdot}68^6$ (due to a) $-0{\cdot}3$ (due to c)).

benzene extract was washed with HCl aq, with $NaHCO_3$ aq and with sat. NaCl. The soln was dried over Na_2SO_4 and the solvent was evaporated. The residue was recrystallized with benzene-hexane (4:1) and gave 575 mg (1·7 mmol, 84% yield) of **1** as prisms. Recrystallization of a small sample from n-hexane gave colorless prisms, m.p. 215·0–215·5°, mass spectrum *m/e* (relative intensity) 338(100), 310(71), 234(21), 233(27), 219(12), 206(28), 205(57), 191(57), 190(15), 189(19), 119(20), 104(13). (Found: C, 88·73; H, 6·76. Calc. for $C_{25}H_{22}O$: C, 88·72; H, 6·55%).

Pseudo-geminal ketone of tetrakis[2.2.2.2]*paraxylylene* (**2**). To a soln of 67 mg (0·15 mmol) carboxytetrakis[2.2.2.2]paraxylylene in 50 ml $CHCl_3$ were added 20 mg of freshly powdered $ZnCl_2$ and 45 mg $POCl_3$. The mixture was stirred at 60° and a small additional amount of $ZnCl_2$ was added after 1 day. After 2 days the mixture was poured onto ice and extracted with $CHCl_3$. The extract was washed with HCl, $NaHCO_3$ aq and NaCl aq. The soln was dried over Na_2SO_4 and the solvent was evaporated. The residue was chromatographed on a silica gel column with n-hexane-chloroform (1:1). The eluted materials were recrystallized from n-hexane and **2** was obtained as pale yellow prisms, m.p. 195–203°, 60 mg (0·14 mmol, 93% yield). Mass spectrum *m/e* (relative intensity) 442(16), 209(13), 168(15), 167(90), 165(22), 149(41), 119(19), 105(100). (Found: C, 89·51; H, 6·54. Calc. for $C_{33}H_{30}O$: C, 89·55; H, 6·83%).

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