# *cis–trans* Isomerism in Bis(trihalogenoacetyl)polymethylbenzenes Resulting from Restricted Rotation about Carbonyl Groups: $^1$H Nuclear Magnetic Resonance Evidence

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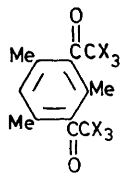
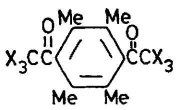
*Summary* The presence of *cis–trans* isomerism at ambient temperatures in bis(trihalogenoacetyl)polymethylbenzenes (**1**)—(**3**) is demonstrated for the first time by the observation of separate $^1$H n.m.r. signals.

We report the first observation of separate $^1$H n.m.r. signals for hindered bis(trihalogenoacetyl)polymethylbenzenes (**1**)—(**3**) resulting in *cis–trans* isomerism from restricted rotation about carbonyl groups at ambient temperatures. The compounds (**1**)—(**3**) (X = Cl or Br) were

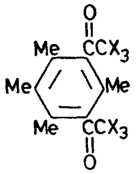


(1)



(2)

a; X = Cl
b; X = Br



(3)

prepared by published methods and their physical properties were checked with those reported; their spectra were in accord with the expected structures. The $^1$H n.m.r. data are given in the Table.

TABLE. $^1$H N.m.r. data[a] on bis(trihalogenoacetyl)polymethylbenzenes.

| | | Solvent | | | |
|---|---|---|---|---|---|
| Compound[b] | Group positions[c] | Benzene | 1-Chloronaphthalene | Δδ[d] | *trans*:*cis* ratio[e] |
| **(1a)** | 2 | 2·23 | 2·16 | — | — |
| | 4,6 | 2·05 | 1·86 | — | — |
| **(2a)** | 2,3,5,6 | 1·96 | 1·89 (*cis*) | 0·13 | 1·4(1·4) |
| | | 1·94 | 1·76 (*trans*) | | |
| **(3a)** | 2 | 2·29 | 2·23 | | |
| | 4,6 | 2·00 | 1·87 (*cis*) | 0·11 | |
| | | | 1·76 (*trans*) | | 1·7(1·7) |
| | 5 | 1·64 (*cis*) | 1·44 (*cis*) | 0·23 | |
| | | 1·58 (*trans*) | 1·21 (*trans*) | | |
| **(1b)** | 2 | 2·45 | 2·36 | | |
| | 4,6 | 2·20 (*cis*) | 2·09 (*cis*) | 0·13 | 2·1(1·9) |
| | | 2·18 | 1·96 (*trans*) | | |
| **(3b)** | 2 | 2·50 | 2·44 | | |
| | 4,6 | 2·15 (*cis*) | 2·01 (*cis*) | 0·13 | |
| | | 2·12 (*trans*) | 1·88 (*trans*) | | 1·7(1·6) |
| | 5 | 1·73 (*cis*) | 1·58 (*cis*) | 0·30 | |
| | | 1·62 (*trans*) | 1·28 (*trans*) | | |

[a] Chemical shifts in δ values from Me$_4$Si internal reference at 60 MHz at 35·0 ± 0·1 °C. [b] Compound (**2b**) was prepared but was too insoluble in solvents used. [c] Positions are numbered with trihalogenoacetyl group as position 1 for (**1**)—(**3**). [d] $\delta_{cis}-\delta_{trans}$; 1-chloronaphthalene solution. [e] Estimated from peak heights and from 0·5 (peak height × width at half-height) (latter values in parentheses) in 1-chloronaphthalene; *trans* form is assumed to be the more stable form. Uncertainty of ±0·1—0·2 estimated. Peak integration was satisfactory for well separated peaks but not for ones slightly overlapping.

Signal separation appears to be qualitatively related to degree of restricted rotation. Thus in the chloro-mesityl case (**1a**) no separation was observed whereas with the bromo-mesityl (**1b**), chloro-duryl (**2a**), and chloro-isoduryl (**3a**) compounds separate signals appear. All *trans* signals appear at higher fields than the corresponding *cis* signals in both solvents. The greatest separations are for the least hindered 5-methyl group in the isoduryl compounds (**3a, b**) but none is evident for the most hindered 2-methyl group in any of the compounds. Differential solvent shielding[1] between *cis* and *trans* isomers (Figure) at certain substituent positions favouring those least hindered would explain this effect. The *trans*:*cis* ratio varies from 1·4 for (**2a**) to 1·9—2·1 for (**1b**). This ratio does not appear to be directly related to the amount of signal separation (Δδ) between isomers.

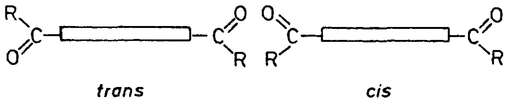


FIGURE. *cis–trans* isomers of bis(trihalogenoacetyl)polymethylbenzenes (side view with plane of ring perpendicular).

A value for free energy of activation [Δ*G*(308 K] for (**2b**) was determined[2] as 78·7 kJ mol$^{-1}$ ± 4·2 (18·8 kcal mol$^{-1}$) (av. of 4 determinations). The value is close to the minima estimated [17 (ref. 3)—23 (ref. 4) kcal mol$^{-1}$] for isomer isolation at ambient temperatures.

Although the first optical resolution of a hindered benzophenone was claimed by Narayanan, *et al.*,[5] Lauer and Staab[6] did not observe n.m.r. signal separation at ambient temperatures for a related compound. Optical resolution of a t-butyl aryl ketone was also reported;[7] rapid racemization was observed with a half-life of 6·2 min at 20·5 °C in chloroform. An angle of 89·9° of the mean plane through the keto-group with the aryl mean plane was reported[8] for an *X*-ray crystallographic study confirming the angle assumed previously[9] for t-butyl mesityl ketone in dipole moment studies. N.m.r. signal separations were not observed[10] for some alkyl aryl ketones at ambient temperatures nor with chiral lanthanide shift reagents.[11]

The authors thank the Robert A. Welch Foundation, Houston, for financial support.

(*Received*, 31*st October* 1977; *Com.* 1134.)

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