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A DYNAMIC NMR STUDY OF RESTRICTED ROTATION OF TWO SUBSTITUTED PHENYL GROUPS IN A *CIS* 1,2-DIPHENYLCYCLOBUTANE

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Abstract: Dimethyl 2,2′,6,6′-tetrachloro-β-truxinate (1) displays restricted rotation of its phenyl groups as evidenced by lineshape analysis of the dynamic ^1H and ^{13}C NMR spectra with the following activation parameters: $\Delta H^{\neq}$ 10.98 ± 0.24 kcal mol^{-1}, $\Delta S^{\neq}$ −4.38 ± 0.99 cal mol^{-1}K^{-1}. In the transition state for rotation the two phenyl groups are perpendicular to one another and the act of rotation involves one phenyl group at a time. The major contribution to the barrier of rotation has its origin in the chlorine atoms. X-Ray analysis of 1 yields a structure with an angle of pucker of 14.3° for the cyclobutane ring in which one chlorine group hovers over the cyclobutane ring while the two chlorines of the other phenyl group avoid the cyclobutane ring.

Spectroscopic and diffraction studies as well as theoretical calculations revealed that some cyclobutanes are planar whereas others are puckered with an angle of pucker of up to 35° and a barrier to ring inversion not exceeding 2 kcal mol^{-1}.[1] The puckering is a result of a balance between a decrease in torsional strain caused by the eclipsing of substituents in the planar ring and the increase in bond-angle strain and 1,3 C···C nonbonded transannular repulsions in the puckered conformation

Numerous tetra-substituted cyclobutanes, obtained by solid-state photodimerization of cinnamic acid derivatives are available.[2] The *cis*-1,2-diphenyl groups in such cyclobutanes could be viewed as belonging to frozen disubstituted ethanes in an eclipsed conformation of a planar cyclobutane or to a gauche conformation of a puckered cyclobutane ring. A simple molecular model[3] of one such compound, dimethyl 2,2′,6,6′-tetrachloro-β-truxinate (1) (Fig.1) indicated that the overcrowding of two bulky 2,6-dichlorophenyl groups in an eclipsed conformation of a planar cyclobutane could lead to restricted rotation about the cyclobutane-phenyl bond. The same is true even if the substituents were assumed to be in pseudoaxial and pseudoequatorial positions in a puckered ring. In fact, the large value of the conformational energy of the phenyl ring (3 kcal mol^{-1})[4] and the large van der Waals radius of the chlorine atom (1.80 Å)[5] support such a proposition. It should also be mentioned that steric hindrance to rotation about sp^2–sp^3 bonds has been observed in compounds with structures reminiscent of our compound 1. Thus α,α,2,4,6-pentachlorotoluene and α,α,α′,α′,2,3,5,6-octachloro-*p*-xylene[6] as well as 2-*c*-methyl-6-*c*-methyl-1-phenylcyclohexanol [7] have barriers to rotation of about 15 kcal mol^{-1}. In the latter type of compound, those in which the 6-methyl or the 2,6-dimethyl group is missing, do not display steric hindrance to rotation.[7] The anticipated hindered rotation can then be observed by the temperature dependence of the lineshape of the aromatic region of the NMR spectra (DNMR). The process is studied in our work not only in the ^1H NMR spectra, but also at two sites in the ^{13}C NMR spectra.

X-Ray Structure Analysis. The X-ray structure analysis of 1 (Fig 2) is invaluable in the interpretation and

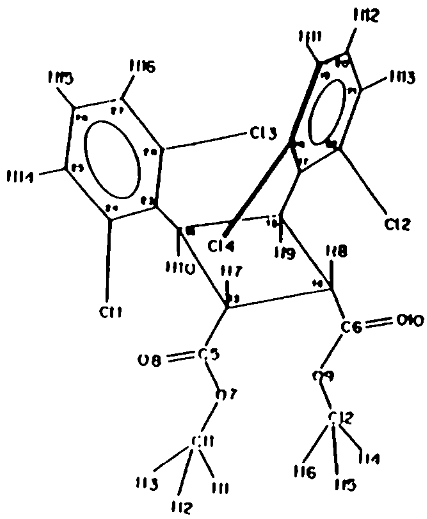


Fig.1. "Perspective" view of 1 with the atomic labels of the X-ray analysis.

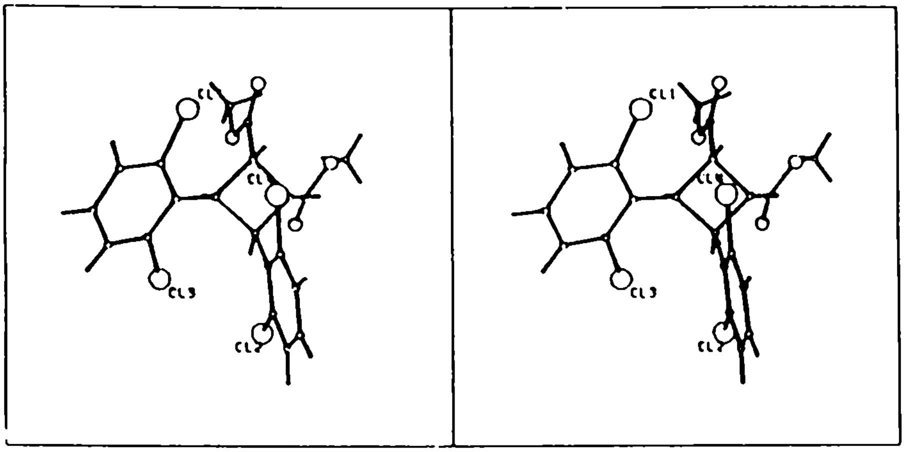


Fig.2. Stereoscopic view of 1 from X-ray structure analysis.

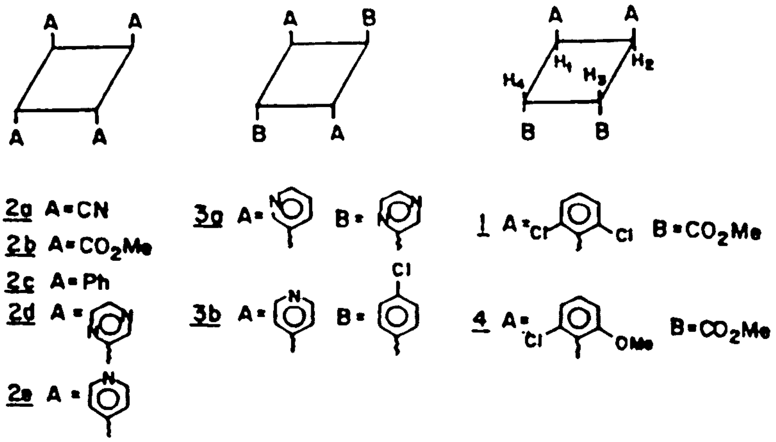
comparison of the NMR and DNMR results obtained in this study.[1a,d] Table 1 lists all cyclobutanes with *cis,trans,cis* configuration for which X-ray structure analysis exists.[10,11] The Table corroborates Margulis's prediction of 1971,[8b] that if the ring is not centrosymmetrically substituted, the cyclobutane will be puckered in the crystal, whereas centro-symmetrically substituted cyclobutanes may still be planar (in 5 of 7 cases in Table 1). His anticipation that cyclobutanes of formula **2** might all be planar in the crystal did not materialize; one of the compounds listed, **2e**, is puckered.

In Table 1 we observe that in cyclobutanes substituted with one or two pairs of aromatic or heteroaromatic rings, these pairs arrange themselves in both the planar and puckered rings, in such a fashion that one aromatic or heteroaromatic ring is diagonally suspended over the cyclobutane ring whereas the other avoids it (with the exception of **2d**) (Fig.3). Models indicate that in such a conformation the nonbonded interactions are at a minimum. We are therefore going to compare the geometry of **1** obtained from our low-temperature static NMR results and the geometry of the transition state of phenyl rotation speculated from the DNMR studies with the geometry of the molecule extracted from the X-ray structure analysis.

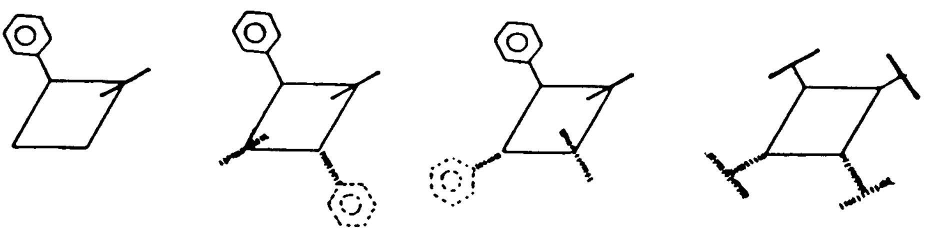
The four bond angles of the puckered cyclobutane ring of **1** fit well with those of planar **2b** and **2c**. Of the four bond lengths, those of $C(CO_2Me)$-$C(CO_2Me)$ (C13-C14) and those of the two *trans* bonds (C13-C16 and

Table 1. Crystallographic data of cyclobutanes with *cis,trans,cis* configuration

Compound	Space group	Z	Symmetry of molecule in crystal	Angle of pucker in crystal	Highest symmetry of free molecule
2a[8a]	$P2_1/n$ (C^5_{2h})	2	C_i	0°	C_{2h}
2b[8b]	$P\bar{1}$ (C^1_i)	1	C_i	0°	C_{2h}
2c[8c]	$P2_1/a$ (C^5_{2h})	2	C_i	0°	C_{2h}
2d[8d]	$C2/c$ (C^6_{2h})	4	C_i	0°	C_{2h}
2e[8d]	$Pccn$ (D^{10}_{2h})	4	C_2	21°	C_{2h}
3a[8d]	$P\bar{1}$(C^1_i)	1	C_i	0°	C_{2h}
3b[8e]	$P2_1/n$ (C^5_{2h})	4	C_1	19.1°	C_{2h}
1[9a]	$C2$ (C^3_2)	4	C_1	14.3°	C_s
4[9b]	$P2_12_12_1$ (D^4_2)	4	C_1	10.7°	C_1 *anti* C_s *syn*



C14-15) are also in line with **2b** and **2c** but the C(Ph)-C(Ph) bond (C15–C16: 1.594 Å) is longer by 0.022 Å than that in **2c** and its cause may be steric because of the large chlorine substituents.[1d] In fact, the average bond length of the bond between the carbons of *cis*-1,2-disubstituted cyclobutanes for a large number of compounds is only 1.559 Å for planar and 1.555 Å for puckered rings.[1d] The overcrowding is also manifested in the larger dihedral angle between the phenyl bonds to the puckered cyclobutane ring which is 20° in **1** and only 5.5° in **2c**, thus the nonbonded distances in **1**, C17–C23 3.25 Å and C22–C28 4.17 Å, are longer than the corresponding ones in **2c**, which are 3.18 and 3.42 Å respectively. This also causes an increase in the nonbonded distances between the chlorines in **1** to 3.43 Å (Cl2–Cl3) and 3.57 Å (Cl1–Cl4). The forced puckering of the ring is then also reflected in the large dihedral angle of the carbomethoxy groups which is 17° in **1**.



Type A Type A1 Type A2 Type B

Fig.3. Type of projection of aromatic and heteroaromatic rings on the "plane" of the cyclobutane ring. Type A: compounds **1** and **4**; type A1: compounds **2c** and **3a**; type A2 compounds **2e** and **3b**; type B: compound **2d**.

compared with 4° in **2b**. The bond lengths and angles of the carbomethoxy groups in **1** also fit with those in **2b**.

Some of the bond angles of the benzene rings of **1** deviate from regular values. Thus the bond angles at the carbons bonded to chlorine (C18, C22, C24 and C28) are in the range of 123.3° to 124.8°, those at the carbons between the chlorines (C17 and C23) have angles of 112.6° and 114.1°, respectively, but those at carbons *ortho* to chlorine on one side only (C19, C21, C25 and C27) are closer to normal, being in the range of 118.7° to 119.6°. Similar observations have been reported and discussed in the literature.[12] Thus it has been observed that the direction of deformation depends on the σ-electron withdrawing and releasing properties of the substituents and the extent of their conjugation with the benzene ring.[12] Electron-withdrawing groups increase the angle at the carbons to which they are bonded in linear dependence on their electronegativity[12b] and decrease similarly the angles *ortho* to them. The opposite is true for electron-releasing groups. In fact, *p*-chlorobenzoic acid[12d] has a bond angle of 122.0° at C-C(Cl)-C and 118.8° *ortho* to it. This is even more impressive in *m*-nitroperchlorylbenzene[13] with an angle of 124.1° at NO_2, 126.1° at ClO_3 and 119.7° and 117.2°, respectively, *ortho* to them, and 113.3° between them. Thus in **1** the much smaller angles at C17 and C23, which are *ortho* to two chlorines at the same time, are due to the enhanced effect of these two chlorines.

^{1}H NMR Spectra. The rotation of the phenyl rings about their bonds to the cyclobutane ring was too slow on the NMR time scale at 270 MHz below *ca* 200 K and their three protons displayed a static ABC spin system (A refers to the proton *meta* to both chlorines and B and C to protons *ortho* to each of them). At higher temperatures mutual exchange of the type ABC $\rightleftharpoons$ ACB was observed and above *ca* 275 K exchange was too fast, yielding an AB_2 system (Table 2 and Fig.4). In the spin analysis of the static and dynamic spectra long range benzylic coupling has been ignored. The collapsed room temperature spectrum yielded a chemical shift difference of $\Delta\delta_{AB}$ 0.103 ppm, close to the value of 0.10 ppm calculated from substituent additivity constants,[14] the B-protons being at the lower field as in the observed spectrum. In 1,3-dichlorobenzene the chemical shift difference is 0.05 ppm, with the protons *ortho* to the chlorines also at lower field.[15] In **1** the *ortho* and *meta* couplings were in the expected range; in 1,3-dichlorobenzene they are 8.10 and 0.89 Hz respectively.[15] The chemical shift differences $\Delta\delta_{AB}$ and $\Delta\delta_{AC}$ increased linearly with temperature over the entire range (Table 2). In the range 163 K to 273 K we find $r(T,\Delta\delta_{AB})$ 0.999, $\Delta\delta_{AB}$ (Hz) = 0.129T − 15.796 and $r(T,\Delta\delta_{AC})$ 0.996, $\Delta\delta_{AC}$ (Hz) = 0.130T − 4.788, which makes $\Delta\delta_{BC}$ practically independent of temperature, as was actually found. All three coupling constants were found not to be affected by temperature. Finally, the chemical shift difference $\Delta\delta_{BC}$ is only *ca* 0.04 ppm (*ca* 11 Hz), too small for assigning the in and out protons.

^{13}C NMR Spectra (Fig.5). In the aromatic region the higher field peaks were assigned to the protonated carbons as NOE enhanced their intensity in the decoupled spectrum. In addition, in each group in the decoupled spectrum below onset of exchange the peak at lower field split into two peaks, indicating that the peak at higher field in each group belongs to a carbon on the rotation axis of the phenyl ring.

^{1}H and ^{13}C DNMR Spectra. Three dynamic processes can be envisaged for **1**: inversion of the cyclobutane ring, torsional oscillation (flip mechanism) (Fig.6),[16,17,18] and rotation of the phenyl rings. Since the first process involves barriers not exceeding 2 kcal mol^{-1},[1b] it is too fast on the NMR time scale to be observed. The second process is nonmutual in the aromatic region: ABC $\rightleftharpoons$ DEF in ^{1}H NMR and involving two spin sys-

Table 2. ^{1}H NMR Parameters of the aromatic protons of 1 and the rate constants of phenyl rotation (from ^{1}H DNMR)[a]

Temp K	δ_A ppm	δ_B ppm	δ_C ppm	$\Delta\delta_{AB}$ Hz	$\Delta\delta_{AC}$ Hz	$\Delta\delta_{BC}$ Hz	J_{AB} Hz	J_{AC} Hz	J_{BC} Hz	k sec^{-1}
163.0	6.974	6.993	7.036	5.19	16.02	11.44	8.34	8.32	1.40	
174.4	6.985	7.009	7.051	6.49	17.60	11.10	8.03	8.04	1.39	
184.2	7.010	7.039	7.079	7.79	18.71	10.92	7.87	7.97	1.30	
205.9	6.984	7.025	7.067	11.07	22.36	11.29	8.24	8.18	1.38	0.9 ± 0.2
215.6	6.982	7.027	7.068	12.23	23.16	10.93	8.00	8.00	1.47	2.8 ± 0.3
225.0	6.976	7.026	7.068	13.68	24.83	11.15	7.99	8.01	1.44	10.0 ± 1.0
234.9	6.973	7.027	7.071	14.74	26.45	11.71	8.20	8.20	1.45	32.0 ± 1.5
244.4	6.970	7.029	7.072	15.85	27.40	11.55	8.08	8.08	1.46	89 ± 6
254.1	6.966	7.030	7.072	17.12	28.58	11.46	8.13	8.19	1.44	189 ± 15
263.5	6.964	7.031	7.073	18.09	29.39	11.31	8.11	8.12	1.45	430 ± 40
273.3	6.958	7.029	7.069	19.13	30.07	10.94	8.09	8.11	1.47	834 ± 100
282.7	6.958	7.053		25.63			8.05			
292.2	6.953	7.052		26.65			8.03			
303.0	6.952	7.055		27.84			7.99			

[a] In CS_2-$CDCl_3$ (3:1) relative to TMS as internal standard.

tems AB ⇌ CD in ^{13}C NMR. Since only mutual exchange of the type ABC ⇌ ACB is observed in the aromatic region of the ^{1}H NMR and two spin systems AB ⇌ BA are similarly observed in the ^{13}C NMR, the process is assigned to the rotation of the phenyl groups. Thus the flip mechanism may also take place but it remains undetectable. Figures 4 and 5 contain the dynamic ^{1}H NMR and ^{13}C NMR spectra of the aromatic region and their computer simulation, respectively. In Tables 2 and 3 are given the appropriate kinetic parameters. The activation parameters for phenyl rotation in 1 and their errors as extracted form the rate constants are as follows: for the ^{1}H spectra (σ_T = 1 K), $\Delta H^{\neq}$ 10.98 ± 0.24 kcal mol^{-1}, $\Delta S^{\neq}$ -4.38 ± 0.99 cal mol^{-1} K^{-1} and $\Delta G^{\neq}$ (298.2 K) 12.29 ± 0.06 kcal mol^{-1}; for the ^{13}C spectra at high field (σ_T = 2 K), $\Delta H^{\neq}$ 11.20 ± 0.75 kcal mol^{-1}, $\Delta S^{\neq}$ -4.12 ± 2.97 cal mol^{-1} K^{-1} and $\Delta G^{\neq}$ (298.2 K) 12.43 ± 0.14 kcal mol^{-1}; for the ^{13}C spectra at low field (σ_T = 2K), $\Delta H^{\neq}$ 10.90 ± 0.32 kcal mol^{-1}, $\Delta S^{\neq}$ -5.30 ± 1.27 cal mol^{-1} K^{-1} and $\Delta G^{\neq}$ (298.2 K) 12.47 ± 0.06 kcal mol^{-1}. The corresponding Eyring plots are displayed in Fig. 7. Details are given in the EXPERIMENTAL. As can be seen from the Figures and Tables, the results obtained from the ^{1}H NMR spectra are more reliable than those from the ^{13}C NMR spectra, as they originate from spectra of a more complex spin system, better resolution and good S/N ratio. By these criteria the ^{13}C NMR spectra are rather poor and their number is small. Furthermore, one of the singlets in the ^{13}C NMR spectra taking part in the dynamic process in the aromatic region at higher field, was partly obscured by another singlet not taking part in that process. Still, the activation parameters obtained from them can be compared for the same dynamic process with those obtained from the ^{1}H NMR spectra, not just at one, but at two sites *(vide infra)*.

As pointed out in the discussion of the X-ray results the molecule in the crystal escapes overcrowding by the chlorine atoms by submitting to a conformation in which only one chlorine hovers over the cyclobutane ring (Figures 2 and 3, type A). Inspection of a model of a single molecule leads to the conclusion that here too minimization of overcrowding can be achieved in the ground state only by a conformation close to that of a molecule in the crystal. Rotating one phenyl group about the C15-C17 bond as axis, while keeping the other phenyl at rest, generates a transition state of least overcrowding of the chlorine atoms when the angle between the two phenyl groups is about 80-85° (Fig.8). A small increase in the angle of pucker of the cyclobutane ring in solution brings the two chlorines further apart in the transition state because of the flexibility of the cyclobutane ring. Consequently the transition state may evolve from rotation of one phenyl ring at a time. This model also shows that concerted conrotation or disrotation will fail as here again severe congestion of

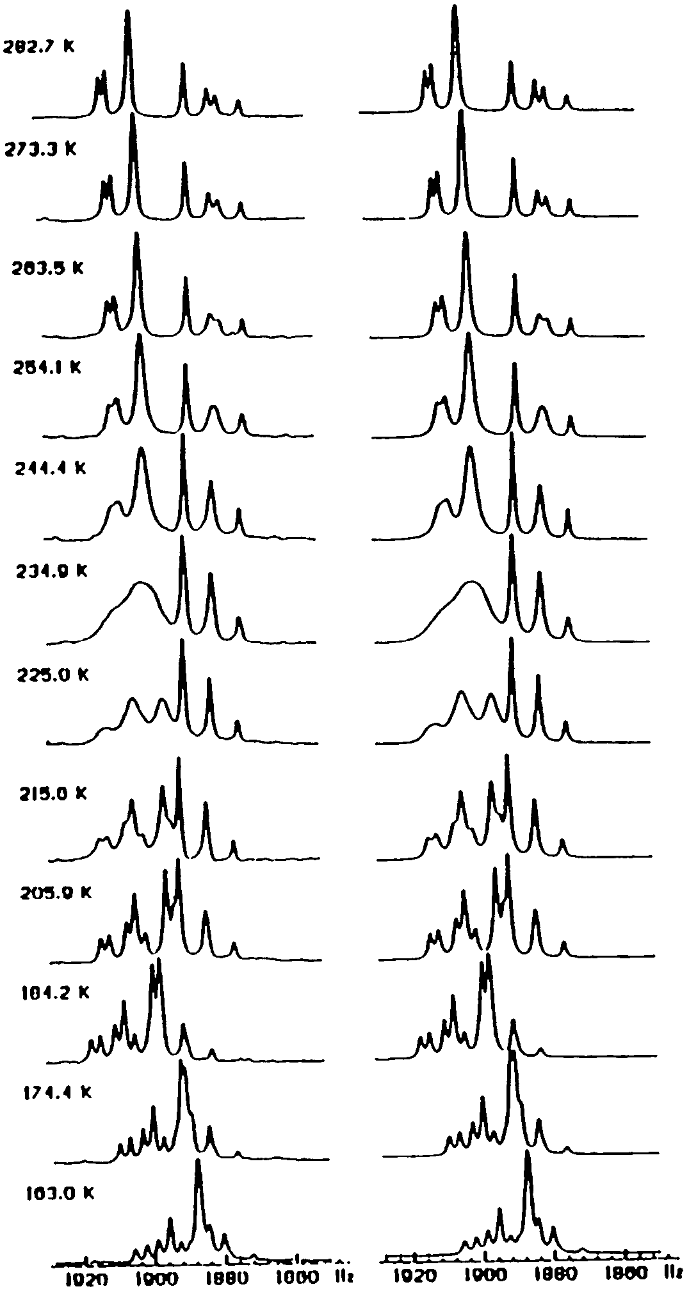


Fig.4. Experimental (left) and computed (right) ^{1}H NMR spectra of the aromatic protons of compound 1.

chlorines and phenyls in a phenyl-phenyl coplanar transition state will ensue. Transition states with perpendicular phenyl groups have also been proposed for phenyl rotation in 1,8-diphenylnaphthalenes.[17,19]

The two *m*-dichlorophenyl groups of 1 are not mutually as congested as the two phenyls of [2.2]paracyclophane, which are also in vicinal positions to each other. This fact is deduced from a comparison between their UV spectra: 1 has a UV absorption very similar to that of *m*-dichlorobenzene,[20] except that it is bathochromically shifted by *ca* 6 nm and has a larger extinction coefficient as a result of its binding to the cyclobutane ring and because two phenyl groups are involved.[21] By contrast, the shape of the UV spectrum of the cyclophane is substantially different.[22] Furthermore, in the cyclophane crystal the closest approach of the two phenyl groups is 2.78 Å,[22,23] whereas in crystals of 1 this intramolecular distance is 3.25 Å, close to the intermolecular distance between stacked aromatic nuclei in crystals which is 3.40 Å.[23] The difference is also manifested in the dynamic behavior of the rings: whereas 1 has to be cooled to −100°C in order to observe its frozen spectrum in the NMR, an optically active [2 2]paracyclophane does racemize at 200°C, albeit only by a methylene-bridge cleaving mechanism.[23,24]

Table 3. Rate constants for phenyl rotation in 1 (from ^{13}C DNMR)[a]

Temp K	High field k sec^{-1}	Low field k sec^{-1}
222.8	5 ± 3	
229.7	12 ± 3	13 ± 5
240.0	40 ± 4	40 ± 8
250.0	85 ± 5	100 ± 8
258.1	165 ± 5	190 ± 10
270.6	790 ± 110	600 ± 75
283.7	1490 ± 350	

It is interesting to compare the value of $\Delta G^{\neq}$ of 1 with those of structures with similar characteristics. The free energies of activation for phenyl rotation via transition states in which the phenyl groups are perpendicular, have been measured and are about 16.5 kcal mol^{-1} for 5a[25a] and 5b.[25b] This value includes a contribution of *ca* 1-3 kcal mol^{-1} [26,27,28] from one nonbonded H···H interaction of the biphenyl type and a contribution of *ca* 13-15 kcal mol^{-1}, originating from the interaction of the two perpendicular phenyl groups. In 1 the free energy of activation is only *ca* 12 kcal mol^{-1}, although it carries chlorine atoms very close to the site of rotation, whereas they are absent in compounds 5. The relative low $\Delta G^{\neq}$ of 1 is a result not only of the fact that a biphenyl type of interaction is missing in the transition state of 1, but mainly because the splaying of the two phenyl rings in crystals of 1 is 68°. This value is only 22° and 35°, respectively, in the two compounds of type 5 of known crystal structure, namely, *peri*-1,8-diphenylacenaphthene[29] and 1,4,5,8-tetraphenylnaphthalene.[30] The average distance between the aromatic carbons in 1 is 5.0 Å, whereas in the above-mentioned compounds it is only 3.7 Å and 3.8 Å, respectively. This geometry assists in the relief of overcrowding in the almost perpendicular transition state of 1 to a much larger extent than in the transition states of compounds of type 5. It seems therefore that the major contribution to $\Delta G^{\neq}$ has its origin in the interaction of the two chlorine atoms from the two adjacent phenyl groups and only to a lesser extent from the interaction of the phenyl groups themselves. The barrier to phenyl rotation in cyclopentyl-2,4,6-trimethylbenzene and its cyclopropyl analog is less than 7.5 kcal mol^{-1} [31] Replacing the methyl groups with chlorines will keep $\Delta G^{\neq}$ for the cyclobutyl analog as low since the van der Waals radii of methyl and chlorine are close in size (2.0 Å and 1.80 Å),[5] as are their volumes and surface areas (13.67 and 12.0 cm^3 mol^{-1}; 2.12 and 1.81X10^{-9} cm^2 mol^{-1}).[32] Only the proximity of two such phenyl groups with bulky chlorine substituents will raise $\Delta G^{\neq}$ by at least 5 kcal mol^{-1}.

Entropies are plagued by much larger errors than free energies and enthalpies.[33,34] Still, the entropy of activation of 1 extracted here from a full lineshape analysis of dynamic ^{1}H NMR spectra may be given some credibility: as pointed out by Binsch *et al.*,[34a] differential effects at the extremes of the dynamic range of the spectra are important. In fact, inspection of our ^{1}H NMR spectra shows that these spectra fulfill this requirement. At the high temperature end we easily observe the gradual sharpening of the doublet at low field and of the quartet at high field with rise in temperature. Positive free entropies of activation were reported for example, for *p*-substituted *N,N*-dimethyl aromatic amides. In this case the perpendicular transition state enjoys larger motional freedom than the planar ground state, because of the partial double bond character of its C-N bond.[35] The small negative $\Delta S^{\neq}$ that we observe in 1 indicates that motional freedom in the perpendicular transition state is somewhat curtailed compared to that in the ground state. This picture, which is in accord

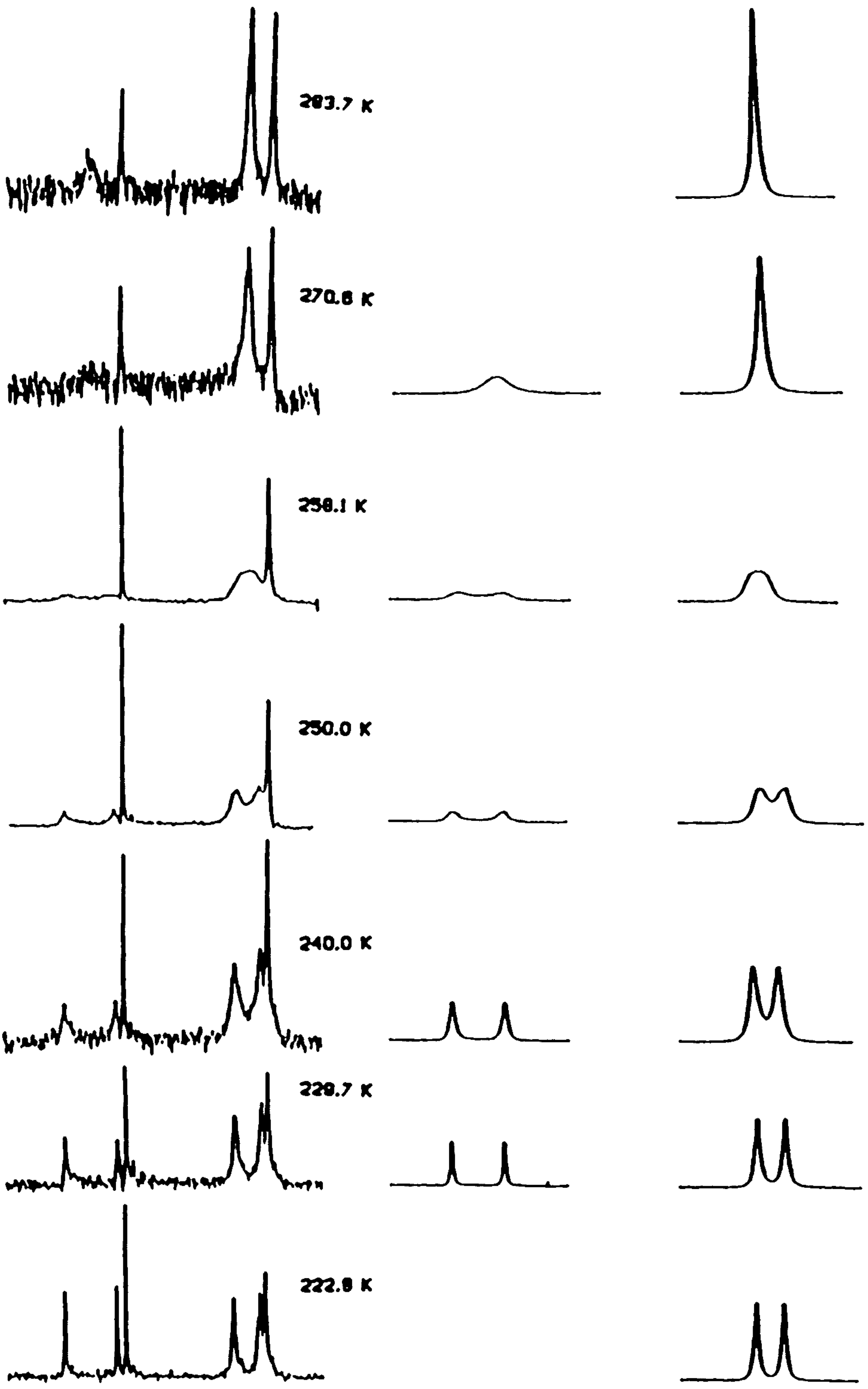


Fig.5. Experimental (left) and computed (middle and right) ^{13}C NMR spectra of the aromatic carbons of compound 1.

with our model of the ground and transition states, also rejects a concerted rotation of both phenyl rings. It does not contradict the conclusion of Jackman and coworkers that in correlated motions entropies of activation are negative but large (-7 to -26 cal mol^{-1}K^{-1}).[36]

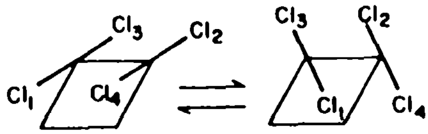


Fig.6. Projection of a flip mechanism of the phenyl rings of compound 1 on the "plane" of the cyclobutane ring.

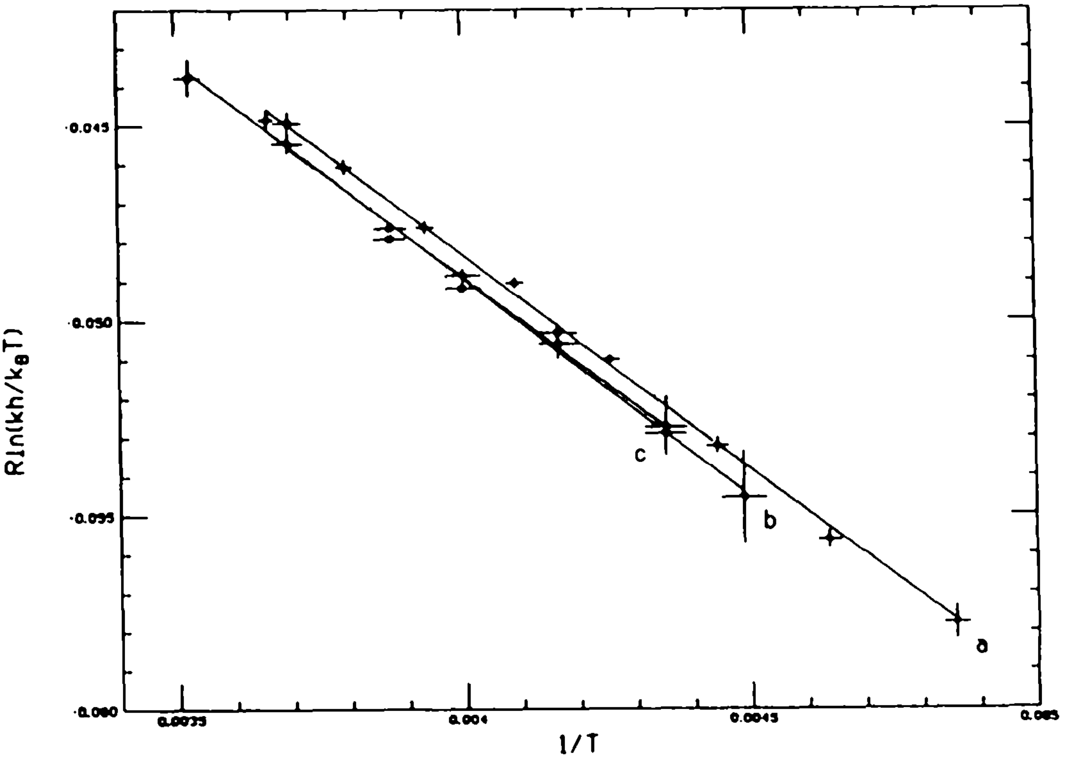


Fig.7. Eyring plots and error bars of phenyl rotation in compound 1: (a) from ^{1}H NMR spectra, (b) from high field ^{13}C NMR spectra and (c) from low field ^{13}C NMR spectra.

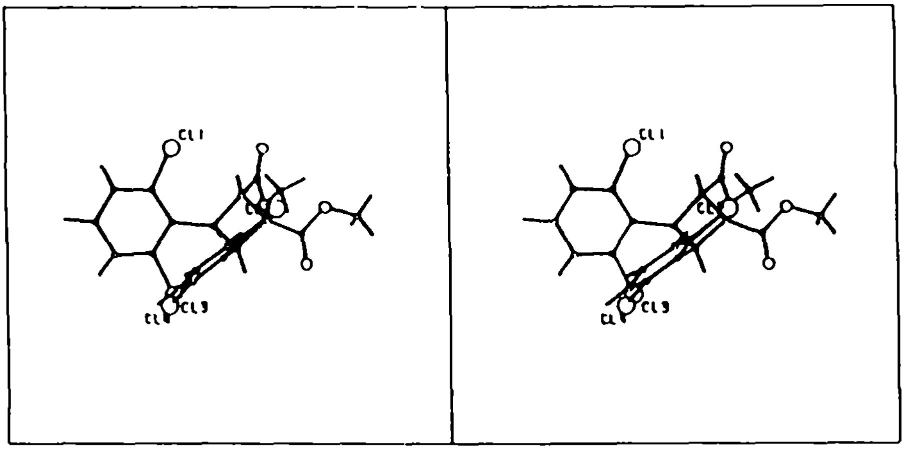
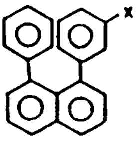


Fig.8. Stereoscopic view of 1 after a 120° rotation of one phenyl ring about the C17-C20 bond of the X-ray crystal structure.



5a X = CMe_2OH
5b X = $CHMe_2$

EXPERIMENTAL

Dimethyl 2,2′,6,6′-tetrachloro-β-truxinate (1) was prepared from 2,2′,6,6′-tetrachloro-β-truxinic acid[37] with diazomethane: mp 116–118°C (iso-PrOH; Fisher-Johns apparatus; uncorrected). UV(MeOH) λ_{max} 269sh, 273sh, 275, 284 nm (ε 430, 504, 542, 418) (Hewlett-Packard 8450A diode array spectrophotometer); [m-dichlorobenzene (EtOH) λ_{max} 250, 256, 263, 270, 278 nm (ε 80, 140, 250, 330, 270)].[20] Anal. Calcd for $C_{20}H_{16}O_4Cl_4$: C, 51.97; H, 3.49; Cl 30.69. Found: C, 52.14; H, 3.59; Cl, 30.19

NMR Spectra were recorded on a Bruker WH-270 NMR spectrometer in the Fourier transform mode operating at 270 (^1H) MHz and at 67.889 (^{13}C) MHz. For ^1H NMR spectra the following data are relevant: 0.02 *M* solution in CS_2–$CDCl_3$ (3:1) in 5-mm o.d. NMR tubes, internal standard TMS, sweep width 2404 Hz, 16 K data points, a pulse with a 90° flip angle, line broadening 0.1 Hz. An inversion-recovery experiment on 4[9b] indicated that all T_1 proton values were less than 1 sec; thus the acquisition time 3.4 sec was sufficient to eliminate saturation effects. The corresponding data for ^{13}C DNMR aromatic region were the following: 0.16 *M* solution in $CFCl_3$-CD_2Cl_2 (5:1) in 10-mm o.d. NMR tubes, 1805 Hz, 16 K, 45° and 0.699 Hz. Broadband decoupled ^{13}C NMR spectra at room temperature in $CDCl_3$ and at ca 190 K in CS_2-$CDCl_3$ (5:1) were also recorded with the above parameters except that the sweep width was 14705.9 Hz. The chemical shift differences in the spectra of methanol[38] and methyl iodide–TMS[39] were used in the determination of temperatures for the ^1H NMR and ^{13}C NMR spectra, respectively.

For spin analysis of the low temperature ^1H NMR spectra of the aromatic region over the entire temperature range program DAVINS[40] was used. For the ^1H DNMR spectra program DNMR5[41] in its simulation and iteration mode was used, but for the ^{13}C DNMR spectra only the first mode was used. The errors in the rate constants were determined by simulation with smaller and larger rate constants until changes in intensity and line shape were beginning to appear. Half the interval between the extreme rate constants was taken as the error. Long range benzylic coupling between the cyclobutane and aromatic protons was ignored in the spin and dynamic analysis. Activation parameters and their errors were computed, using the Eyring equation, with a linear regression – least squares program based on equations in the literature.[42] These equations weight the errors in both the temperatures and rate constants

X-Ray crystallographic data. Crystals for X-ray analysis were obtained from $CHCl_3$-iso-PrOH. $C_{20}H_{16}O_4Cl_4$, M = 462.160, monoclinic, space group C2, a = 11.172(1) Å, b = 19.905(1) Å, c = 10.294(1) Å, $\beta = 119.36(1)°$, V = 1995.1 Å^3, Z = 4; calculated density 1.54 gcm^{-3}. The measurements were done at 95 K. The intensities of all reflections were measured according to the ω-2θ technique by using a scan range of 1° and constant scan speed of 2° per min on an Enraf-Nonius CAD-4 automatic diffractometer (MoK_α radiation, $\lambda = 0.7114$ Å). The structure was solved by direct methods using SHELX-86.[43] A set of 2217 reflections was used in all calculations with $|F_0| > 3\sigma |F_c|$. Empirical absorption correction was applied ($\mu = 8.55$ cm^{-1}).[44] The non-hydrogen atoms were refined anisotropically. All hydrogens were located on a difference Fourier map, and positional and thermal parameters were refined. A final difference Fourier map possessed no special features. Final R values are R = 0.038, $R_w = 0.041$. Tables of fractional atomic coordinates of C, O, and H atoms, anisotropic temperature (thermal) factors, bond lengths and bond angles are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CC2 1EW, England. Any request should be accompanied by the full literature citation for this paper.

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