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STERIC AND ELECTRONIC CONTRIBUTIONS TO BARRIERS OF INTERNAL ROTATION IN 1,8-DIBENZOYLNAPHTHALENES

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Abstract—Restricted rotation about the naphthalenyl–carbonyl bonds in the title compounds results in mixtures of *cis* and *trans* rotamers, the equilibrium and the rotational barriers depending on the substituents. For 2,7-dimethyl-1,8-di-(p-toluoyl)-naphthalene (1), $\Delta H^\circ = 3.66 \pm 0.14$ kJ mol^{-1}, $\Delta S^\circ = 1.67 \pm 0.63$ J mol^{-1} K^{-1}, $\Delta H^{\neq}_{tc} = 55.5 \pm 1.3$ kJ mol^{-1}, $\Delta H^{\neq}_{ct} = 51.9 \pm 1.3$ kJ mol^{-1}, $\Delta S^{\neq}_{tc} = -41.3 \pm 4.1$ J mol^{-1} K^{-1} and $\Delta S^{\neq}_{ct} = -42.9 \pm 4.1$ J mol^{-1} K^{-1}. The rotation about the phenyl–carbonyl bond requires $\Delta H^{\neq} = 56.9 \pm 4.4$ kJ mol^{-1} and $\Delta S^{\neq} = -20.5 \pm 15.3$ J mol^{-1} K^{-1} for the *cis* rotamer, and $\Delta H^{\neq} = 43.5 \pm 0.4$ kJ mol^{-1} and $\Delta S^{\neq} = -22.4 \pm 1.3$ J mol^{-1} K^{-1} for the *trans* rotamer. The role of electronic factors is likely to be virtually the same for both these rotamers but steric interaction between the two phenyl rings occurs in the *cis* rotamer only. Hence, the difference of the activation enthalpies obtained for the *cis* and *trans* rotamers, $\Delta\Delta H^{\neq} = 13.4$ kJ mol^{-1}, provides a basis for the estimation of the role of steric factors in this rotation. For the tetracarboxylic acid 2 and its tetramethyl ester 3 the equilibrium is even more shifted towards the *trans* form because of enhanced steric and electrostatic interactions between the substituents in the *cis* form. The barriers for the rotation around the phenyl-carbonyl bond and the *cis-trans* isomerization are lowered; an explanation for this result is presented.

The barriers of internal rotation have their origin in both steric and electronic factors. The former occur in crowded molecules and the latter are typical for conjugated bonds. It can be anticipated that both these types of interaction are operative in 2,7-dimethyl-1,8-di-(p-toluoyl)-naphthalene (1, Scheme 1). Indeed, the mobility of each of the toluoyl substituents is obviously sterically hindered by the naphthalene 2- or 7-methyl group and by the twin *peri* substituent whereas conjugation of the carbonyl group with both the benzene and naphthalene aromatic system affects the barriers to rotation about the C(O)–Ar bonds by its influence on their bond order.

The aim of the present work was to investigate the rotational equilibria in the title compounds and to estimate the role of the two factors mentioned. Of particular interest was the possibility of estimating the steric contribution to the barrier to rotation about the C(O)–Ph bonds in the *cis* rotamer.

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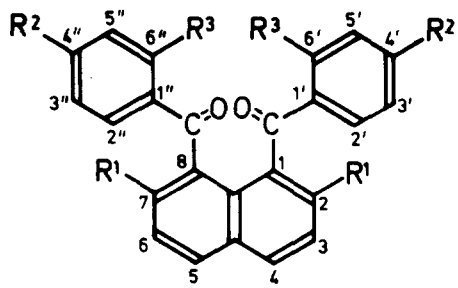
RESULTS AND DISCUSSION

The 360 MHz spectrum of 1 recorded at 320 K (Fig. 1a) shows broadened signals in both the aliphatic and aromatic region suggesting slow intramolecular motions. The spectrum of the totally frozen system presented in Fig. 1(d), and the spectral changes occurring in the intermediate temperature range can be interpreted in the following way. The rotation around the C(1)–C(O) and C(8)–C(O) bond is frozen at 245 K (Fig. 1b) resulting in a *cis-trans* isomer pair (1c, 1t), the population distribution



Compound	R^1	R^2	R^3
1	Me	Me	H
2	COOH	COOH	H
3	COOMe	COOMe	H
4	H	H	Me

Scheme 1.

being 17:83 according to integration of the methyl signals. The rotation about the C(1')–C(O) and C(1'')–C(O) bond is also frozen at this temperature for one of these isomers, as reflected by the sharp signals of the ABMX type in the aromatic region, but still rapid for the other one. The signals of the latter split below *ca* 238 K and sharpen at even lower temperatures yielding another ABMX spectrum (Figs. 1c, d).

The signals of lower intensity are attributed to the *cis* isomer on both thermodynamic and kinetic arguments. The energetically unfavourable interaction between phenyl rings in 1,8-diphenylnaphthalene derivatives[1–3] is supplemented in **1c** by the repulsion between the carbonyl groups and between the 4' and 4'' methyl groups but this strain is greatly relieved in **1t** (*cf* Fig. 2). The *cis* rotamer is also expected to have a higher barrier to rotation about the C(1')–C(O) and C(1'')–C(O) bond, i.e. to be frozen first, because the electronic restriction must be roughly the same as in the *trans* rotamer, but steric hindrance is obviously much higher due to the juxtaposed phenyl rings. Experimentally, these conclusions were corroborated by the growth of the signals of the assumed *trans* rotamer at the expense of the signals of the more polar *cis* rotamer on going from the polar solvent dichloro methane ($\mu = 1.6$ D) to the nonpolar carbon disulfide.

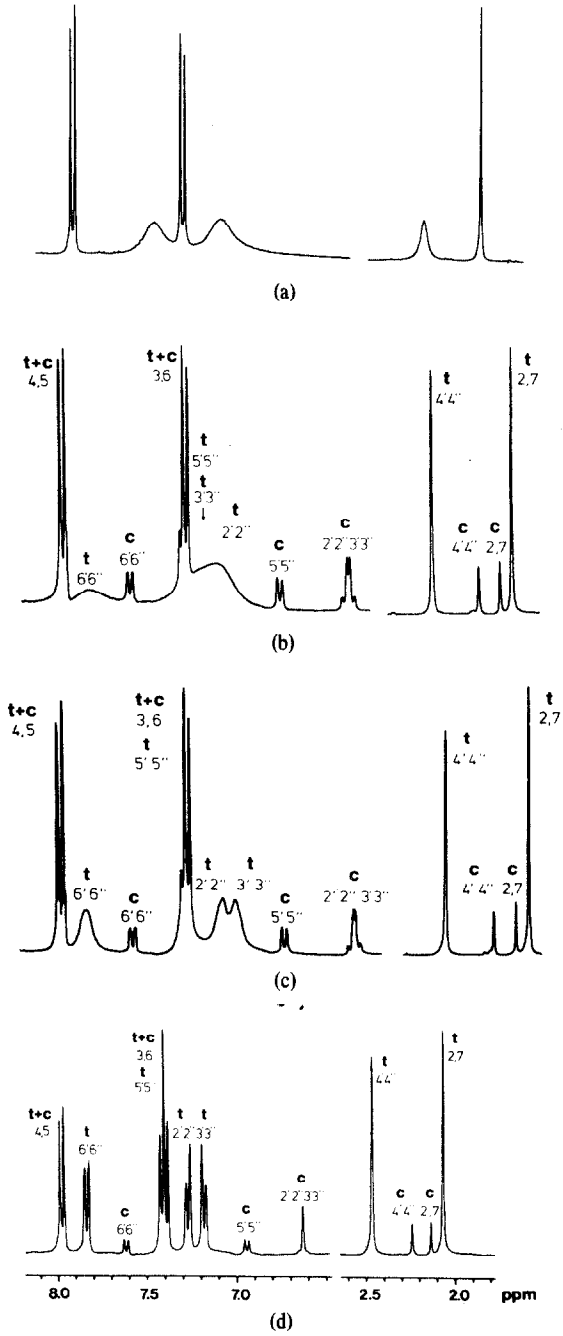


Fig. 1. Temperature-dependent ^{1}H NMR spectra of **1** at (a) 320 K, (b) 245 K, (c) 230 K and (d) 190 K. For enumeration see Scheme 1.

The assignments of the spin systems indicated on the spectrum (Fig. 1) were based on decoupling and saturation transfer experiments as well as on commonly accepted electronegativity and anisotropy (ring current) arguments. For example, the *t*3'3'' and *t*2'2'' protons were discriminated by the benzylic long-range coupling of the former with the *t*4'4'' methyl protons. In turn, the *t*2'2'' signals, which show a well resolved meta coupling of 1.4 Hz, were readily distinguished from the equally split *t*6'6'' ones on grounds of chemical shifts since the former are expected to be shifted upfield by the naphthalene ring current (*cf* Fig. 2). The *t*5'5'' signal, which is overlapping with the naphthalene 3,6-protons signal, was found by decoupling from the *t*6'6'' protons. The resonances of the *cis* rotamer were assigned in a similar manner. All assignments were confirmed by saturation transfer, e.g. irradiation of the *t*6'6'' protons before each scan resulted in a decreased intensity of the *t*2'2'' signal.

The static parameters for the exchange-broadened spectra were obtained by extrapolation from the slow-exchange region. The chemical shifts of the *c*6'6'' and *t*6'6'' signals were only slightly temperature-dependent and the marked drifts of all other signals showed a trustworthy linearity characterized by high correlation coefficients (Table 1). Although the chemical shifts of the aromatic protons of the *trans* isomer could only be determined experimentally in a narrow temperature interval between 181 and 225 K and had to be extrapolated as far as up to 300 K, the excellent correlation of the Eyring plot (Fig. 5b) seems to indicate that linearity was preserved in the region of exchange-broadening. The populations, determined by electronic integration, were treated in a similar way.

Since the errors of integration, estimated at relative 3%, exceeded the errors of the static parameters by more than one order of magnitude, the latter were disregarded when calculating a weighted least-squares fit[4] of the equilibrium constant, $K(c \rightleftarrows t)$, to the standard thermodynamic equation (Fig. 3). The thermodynamic quantities thus obtained were $\Delta H^0 = 3.66 \pm 0.14$ kJ mol^{-1} (874 ± 34 cal mol^{-1}) and $\Delta S^0 = 1.67 \pm 0.63$ J mol^{-1} K^{-1} (0.40 ± 0.15 cal mol^{-1} K^{-1}).

Theoretical dynamic bandshapes were computed using the DNMR3 program[5] and visually compared with the experimental spectra. Both the unresolved long-range benzylic couplings and the phenylic meta couplings of 1.4 Hz were disregarded, as their contribution to the exchange-broadened spectra was insignificant. The *cis*–*trans* isomerization rates were determined from the 4'4''-methyl signals for which the problem was treated as a two-configuration nonmutual exchange. The band-shapes for the aromatic region were calculated according to the exchange matrix shown in Fig. 4. The details underlying

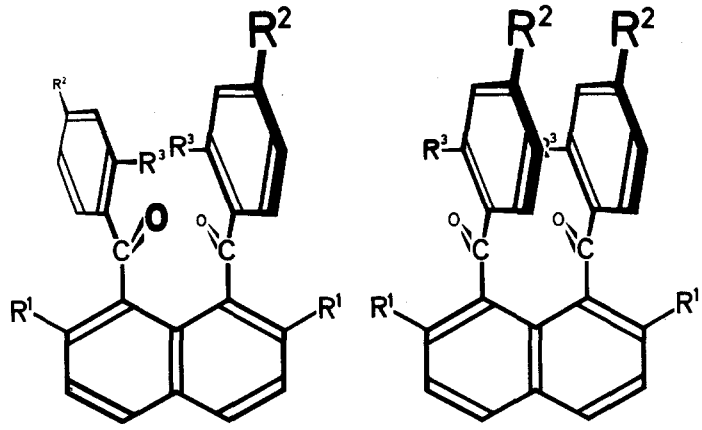


Fig. 2. Perspective views of the *trans*(left) and *cis* forms of compounds 1–4 (for substituents, see Scheme 1).

the matrix formalism were described by Höfner *et al.*[6] The $(AB)_t \overset{k_t}{\rightleftarrows} (CD)_t$ and $(EF)_c \overset{k_c}{\rightleftarrows} (GH)_c$ exchange schemes are self-explanatory but the remaining processes seem to require some comments. It is easily seen, that the phenyl ring which jumps to the opposite side of the naphthalene ring in the course of the *cis-trans* isomerization must simultaneously be rotated by π around the C(1')–C(O) or C(1")–C(O) bond when passing at the 2- (or 7-) naphthalene methyl substituent. As a consequence, one half of each pair of equivalent phenylic protons (e.g. *t*2' of *t*2'2" of AB) not only changes its label from *t* to *c* but also migrates to the opposite site of this phenyl ring (to the position *c*6' for the above example). Numerically, this corresponds to the AB⇄GH exchange with 1/2 of the rate constant of the $c \rightleftarrows t$ process as determined from the methyl signals, for which the rotation about the C(1')–C(O) and C(1")–C(O) bonds is irrelevant. Simultaneously, the other half of this pair, *t*2", belonging to the non-moved benzenoic ring, changes its label to *c*2", this change being tantamount to the AB⇄EF transition, again with 1/2 of the rate constant k_{tc}. Similar considerations apply to all the remaining protons and transition paths.

No attempt to apply the iterative DNMR5 version of the program[7] was undertaken because of the problems ensuing from the partial overlap of the signals of the benzene and naphthalene ring protons. On the other hand, it would have been virtually impossible to fit the curves when varying three rate constants simultaneously. Fortunately, the k_{ct} constant was independently deter-

Table 1. Temperature dependence of the chemical shifts of Compound 1

Protons[a,b]	Temperature range (K)	Drift (Hz)	r[c]
c'4"	181 - 260	10.0	0.9978
t'4'4"	181 - 260	13.0	0.9974
c2'2"	195 - 235	5.0	0.9935
c3'3"	195 - 255	10.3	0.9899
c5'5"	181 - 275	9.8	0.9876
c6'6"	181 - 275	1.8	
t2'2"	181 - 225	22.3	0.9958
t3'3"	181 - 225	16.7	0.9963
t6'6"	181 - 225	2.2	

[a] For labelling, see Scheme 1 and Fig. 4. [b] t5'5" not determined because of overlap with naphtalene proton signals. [c] Correlation coefficients of the linear drift of chemical shifts.

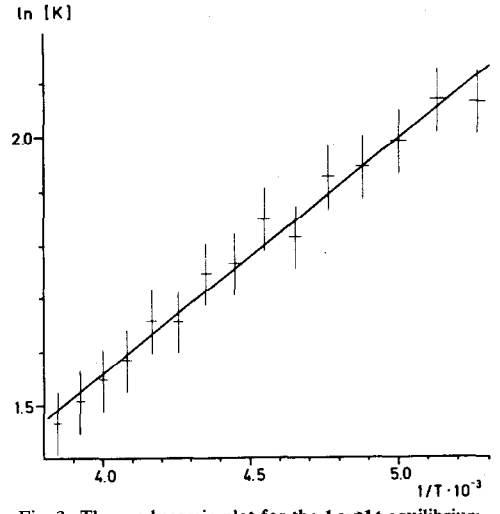


Fig. 3. Thermodynamic plot for the $1c \rightleftarrows 1t$ equilibrium.

$(AB)_t$	k_t	$\frac{1}{2}k_{ct}$	$\frac{1}{2}k_{ct}$
k_t	$(CD)_t$	$\frac{1}{2}k_{ct}$	$\frac{1}{2}k_{ct}$
$\frac{1}{2}k_{tc}$	$\frac{1}{2}k_{tc}$	$(EF)_c$	k_c
$\frac{1}{2}k_{tc}$	$\frac{1}{2}k_{tc}$	k_c	$(GH)_c$

Fig. 4. Schematic representation of the exchange matrix for the computation of the bandshapes of 1. The exchanging spin systems are labelled as follows: $(AB)_t$ = *t*2'3' and *t*2"3", $(CD)_t$ = *t*6'5' and *t*6"5"; $(EF)_c$ = *c*2'3' and *c*2"3"; $(GH)_c$ = *c*6'5' and *c*6"5".

mined from the analysis of the methyl signals. Regarding the two remaining processes, described by k_t and k_c, advantage can be taken of the fact, that the former, which is faster by two orders of magnitude, has indirectly some effect, *via* alternative paths, on the magnetization transfer between the states directly related by the smaller k_c constant (i.e. between EF and GH) but the reverse effect of the slower process on the faster one is negligible. Hence, by fitting first the signals of the *trans* isomer and putting the k_t constants thus found (as well as the k_{ct} ones determined as mentioned above) into the computation scheme for k_c, the best possible result could be obtained with a strongly reduced number of steps of the trial-and-error procedure. The weighted least-squares fits[4] of the rate data to the Eyring equation are shown in Fig. 5(a–c) and the activation parameters are listed in Table 2.

The literature data on restricted rotation in benzophenones is too scarce to allow more than qualitative comparisons with the present material. In the early work from our laboratory the barriers to rotation about the phenyl–carbonyl bond ranged from $\Delta G^{\neq}_{206} = 17.7 \pm 0.2$ kcal mol^{-1} for 3,5-dimethyl-2′,4′,6′-tritert-butyl-benzophenone[8] to $\Delta G^{\neq}_{207} = 10.0 \pm 0.2$ kcal mol^{-1} for the corresponding 2′,4′,6′-tri-isopropyl derivative.[9] Since the rotation of the ring containing smaller ortho substituents is energetically favoured, the above values can formally be confronted with that obtained for the rotation of the phenyl rings of **1***t* ($\Delta G^{\neq}_{207} = 11.5$ kcal mol^{-1}). In this comparison, two ortho isopropyl groups seem to offer smaller resistance to rotation of the other ring linked to the carbonyl than one ortho methyl and one peri carbonyl groups do; but with two ortho tert-butyl groups the opposite is true.

Of greater interest is the barrier to rotation of the phenyl rings in **1***c*. According to X-ray analysis[10] these two rings are arranged nearly parallel at a distance ranging from 328 pm (C2′ ··· C2″) to 408 pm (C5′ ··· C5″). It can be assumed that the ground-state geometry of the molecule does not change much in solution because the interactions between the phenyl rings and the 2,7-methyl substituents, as well as between the two oxygens, probably prevent too great a spreading of the angle between these rings. The steric hindrance encountered here is of considerable interest in connection with the work on cyclophanes being made in our laboratory. It can be attempted to estimate the steric contribution to this barrier by comparing it with that found for the *trans* isomer. The electronic factors can be assumed to be practically equal for both isomers whereas the steric ones related to the interaction between the phenyl rings, only contribute in the case of the *cis* isomer. If no other steric hindrance occurred in the *trans* isomer, the difference obtained by subtracting the free activation energy determined for *t* from that established for *c*($\Delta\Delta G^{\neq} = 3.2$ kcal mol^{-1}) could be taken as a measure for the steric resistance to rotation in **1***c*. However, there is some additional steric interaction in **1***t* lacking in **1c**, namely, that between the 2′,6′- (and 2″, 6″) ortho protons and the oxygens of the 8- (and 1-, respectively) carbonyl groups; hence, the steric contribution calculated in this way for **1***c* is obviously underestimated, i.e. the value obtained should be considered as the lower limit. The upper limit can roughly be estimated on the basis of the value for the 1,8-diphenylnaphthalene system,[3] $\Delta G^{\neq}_{298} = 14.9$ kcal mol^{-1}. This barrier can be considered as composed of the share attributable to steric interaction between

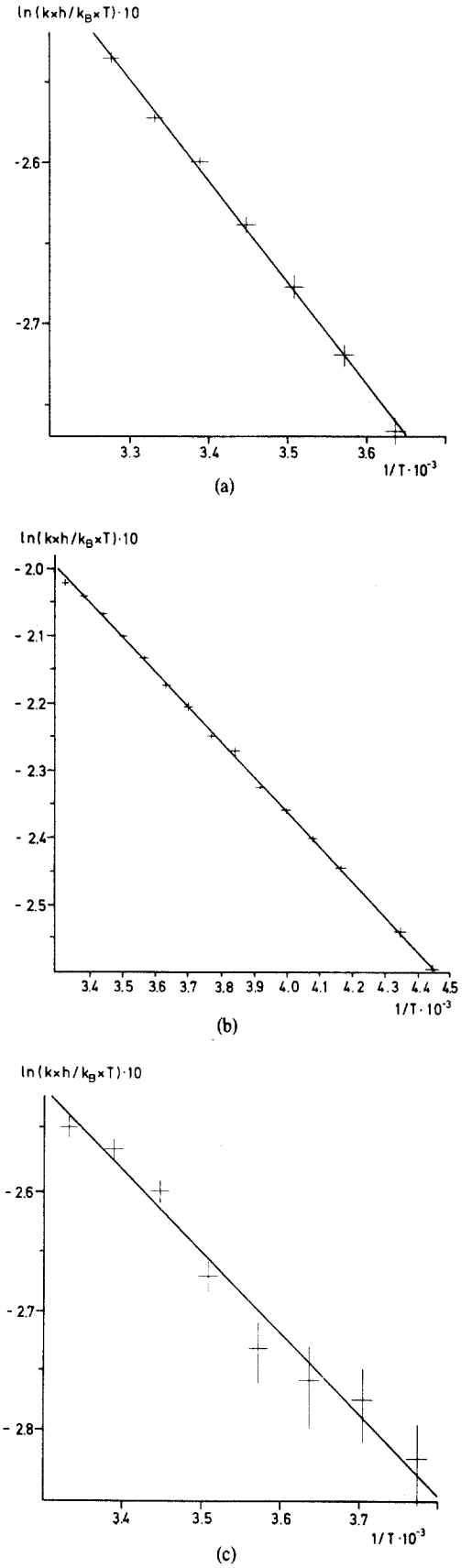


Fig. 5. Eyring plots for the rate data on (a) $k_{ct} + k_{tc}$, (b) k_t and (c) k_c of **1** (for notation, see Fig. 4).

Table 2. Activation parameters for the restricted rotations in Compound **1**

Rate constant[a]	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ J mol^{-1}K^{-1}	$\Delta S^{\neq}$ cal mol^{-1} K^{-1}	r[b]	$\Delta G^{\neq}_{207}$ kcal mol^{-1}
k_{tc}	55.5 ± 1.3	13.3 ± 0.3	-41.3 ± 4.1	-9.9 ± 1.0	0.9994	
k_{ct}	51.9 ± 1.3	12.4 ± 0.3	-42.9 ± 4.1	-10.3 ± 1.0	0.9994	
k_t	43.5 ± 0.4	10.4 ± 0.1	-22.4 ± 1.3	-5.4 ± 0.3	0.9967	11.5
k_c	56.9 ± 4.4	13.6 ± 1.1	-20.5 ± 15.3	-4.9 ± 3.7	0.9895	14.7

[a] For notation, see Fig. 4. [b] Correlation coefficient of the fit.

the two phenyl rings plus a part related to electronic and steric hindrance of the biphenyl type. Hence, by subtracting the barrier for the perpendicular conformation of diphenyl[14] ($\Delta G^{\neq}$ = 4–5 kcal mol^{-1}) one obtains 10–11 kcal mol^{-1} as the upper limit for the steric part of the barrier for **1***c*. The true value is likely to be considerably lower owing to more flexibility in **1***c* compared to 1,8-diphenylnaphthalene.

In spite of all the limitations of splaying of the two phenyl rings in **1***c*, the analogy with cyclophanes remains a remote one, however. The large difference in rotational barriers (e.g. $\Delta G^{\neq}$ = 33.5 kcal mol^{-1} for a [3.4]-paracyclophane[12]) can be accounted for by deformations of both the substituents and the naphthalene ring in **1***c* enabling the system to partly escape the strain in the transition state. These factors were considered to be responsible in part for the low barriers in *peri*-phenylnaphthalenes.[3] On the other hand, the suggested[3] additional role of the ground-state strain seems questionable since the transition-state strain in the same structure fragment must obviously be even higher. The comparison[3] with several atropoisomers lacking this ground-state strain is hardly convincing, as their higher barriers can plausibly be explained by the interaction between the large *o,o'*-substituents, i.e. by the transition-state strain in a structure fragment that has no counterpart in those *peri*-substituted naphthalenes.

The large negative activation entropies for all three rotations can tentatively be explained by limitations of the motional freedom resulting from enhanced steric strain in the transition state.

The low rotational barriers for compounds **2**–**4** prevented a rigorous treatment, but semiquantitative comparisons were nevertheless informative (Tables 3, 4 and Fig. 6). Thus, the equilibrium shift towards the *trans* form for **2** and **3** as compared with **1** (*ca* 97, 93 and 89%, respectively, at 190 K) is obviously due to electrostatic and enhanced steric interactions between the carboxy or ester groups in **2***c* and **3***c*, respectively.

The barriers are evidently smaller for **2** and **3** than for **1** since broadening and coalescence of the corresponding signals, spaced at comparable $\Delta\nu$ intervals, occur at temperatures lower than those for **1** by *ca* 20° in the case of **2** and **3**. The lower barrier to rotation about the phenyl–carbonyl bond is readily explainable in terms of electron attraction by the electronegative *para* carboxy or ester groups resulting in decreased C(1′)–C(O) and C(1″)–C(O) bond orders. It might seem at a first glance that the barrier for the naphthyl–carbonyl bond should be *enhanced* for the same reason, because the planes of the carbonyl groups are nearly perpendicular to the naphthalene system in the ground state[10] and coplanar in the transition state. However, the 2,7-carboxy or carbomethoxy groups are unlikely to affect the π bond order of the naphthalenyl-carbonyl bonds because of the synchronous loss of their coplanarity with the naphthalene group while 1- or 8-carbonyl groups become coplanar. Since, on the other hand, each elementary act of the *cis-trans* isomerization includes the rotation about the phenyl–carbonyl bond, the net effect of replacing the methyls by the carboxy or carbomethoxy groups can be expected here to be qualitatively the same as for the latter rotation, i.e. the barrier for the $c \rightleftarrows t$ half-rotation should also be lower. Although the twist of the carboxy or carbomethoxy group and the resulting loss of their conjugation energy calls for some correction of this net lowering of the barrier, it can be assumed that this contribution is small, in accordance with the known minor tendency of those groups for conjugation. Simultaneously, their inductive effect can be expected to enhance the flexibility of the naphthalene framework, thus contributing to the lowering of the barrier. There is one more factor that possibly contributes to the lowering of this barrier, namely, the ground-state strain originating from the shorter distance between the carbonyl and one of the oxygens of the 2-substituent in **2** or **3**, than was the gap between the carbonyl and the 2-methyl group in **1**. Whereas the weaker interaction in **1** allows the 1-substituent to assume the value of 73.4° of the angle between its 1-CO-1′-plane and the naphthalene rings,[10] the stronger repulsion in **2** and **3** would enforce its further twist towards the right-angle position, thus causing a complete loss of conjugation of the carbonyl with the naphthalene system. This contribution, although obviously not large, can still be noticeable since $\cos^2 73.4 = 0.08$. Admittedly, this explanation is tentative.

For compound **4** only averaged spectra could be obtained. Although all phenylic proton signals gradually broadened on lowering the temperature, the rotation was still far from being frozen at 208 K. This was not un-

Table 3.[a] Chemical shifts for compounds 1–4

Compound	1	2	3	4
Signal T(K)	190	187	187	300
c2'2"	6.654		6.745	7.201[b]
t2'2"	7.278	7.608	7.491	
c3'3"	6.628		7.381	7.167[b]
t3'3"	7.188	8.099	8.029	
c4'4"	2.243		3.867	7.364[b]
t4'4"	2.466		3.948	
c5'5"	6.951		7.747[c]	7.440[b]
t5'5"	7.427	8.233	8.230	
c6'6"	7.618		7.793[c]	2.417[b]
t6'6"	7.852	7.952	7.956	
c2,7	2.139		3.643	7.507[b,d]
t2,7	2.072		3.500	
c,t 3,6	7.387	8.574	8.303	7.520[b,d]
c,t 4,5	7,967[e]	8,361	8,212	8.079[b,d]

[a] For labelling, see Scheme 1. [b] c+t, averaged. [c] The assignments c5'5" and c6'6" might possibly be reversed. [d] Simulated-iterated using the Bruker PANIC program. [e] c4,5 was resolved here (7.963 ppm).

Table 4.[a] Coupling constants for compounds 1–4

Compound	1c	1t	2t	3c	3t	4c,t
J_{ij} T(K)	190		187	187		300
2'3'	7.9	7.9	8.2	7.9	7.9	7.7
2'4'						1.3
2'6'	b	1.4	1.4	b	b	
3'5	b	1.4	1.7	b	b	7.7
5'6'	7.9	7.9	8.2	7.2	8.1	
23						7.04[c]
24						1.16[c]
34	8.4	8.4	8.6	b	8.6	8.49[c]

[a] For labelling, see Scheme 1. [b] Not resolved. [c] Simulated-iterated using the Bruker PANIC program.

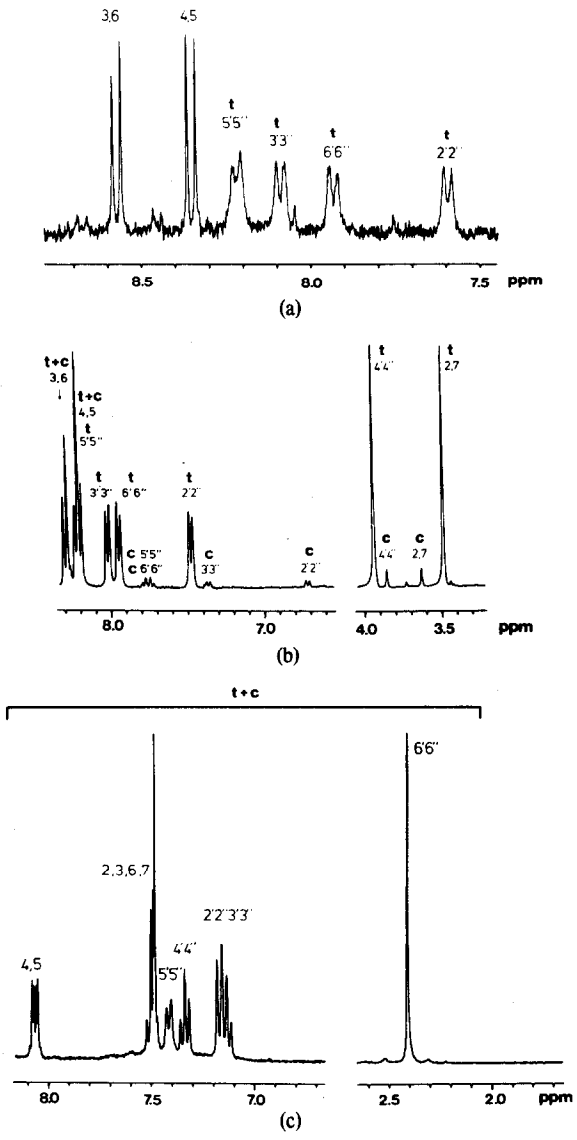


Fig. 6. ^{1}H NMR spectra of **2** (top; 187 K), **3** (187 K) and **4** (bottom, 300 K). For labelling, see Scheme 1.

expected since, contrarily to what occurred with 2,7-dimethyl substituted compounds **1–3**, no methyl group was involved in steric interactions in the critical 2/2′ and 7/2″ fragments during the *cis-trans* isomerization, because both R^3 methyls were located "up" (as shown in Fig. 2) due to their extremely strong interaction with the naphthalene ring in the alternative "down" position.

EXPERIMENTAL

The synthesis of compounds **1–4** will be described elsewhere.[13] NMR spectra were recorded at 360 MHz in Fourier transform mode using a Bruker HX-360 spectrometer equipped with a Bruker Aspect 2000 computer. The spectral width was 3.3 kHz, and 16 K data points were used. Hence, the acquisition time was 2.5 s and digital resolution amounted to 0.4 Hz. A 30° flip angle was applied. Since all T_1 relaxation times (estimated by nulling of the signals during inversion-recovery sequences) were below 1 s, the pulse interval of 2.5 s was more than sufficient for avoiding saturation effects.

The 5% solutions in dichloromethane-d_2 containing traces of TMS were carefully degassed and sealed under Helium in precision 5-mm-o.d. NMR tubes. The spectra were measured in the whole temperature range at 5° intervals without taking the sample out of the magnet. The temperature unit was calibrated with a standard methanol NMR thermometer before and after each of such series of measurements. The errors of the temperature measurements are believed to lie within ±1°.

The calculations of the theoretical spectra were carried out on a IBM 370/168 computer at the Rechenzentrum of the University of Heidelberg. Some details and the relevant references were indicated in the Results and Discussion Section. The effective transverse relaxation time was determined by measuring the linewidth of the TMS signal and assumed to apply to all other signals as well. Since the linewidth of the 2,7-methyl signal, which was not exchange-broadened, was identical within experimental error at 190 and 320 K, a constant T_2^* value could be used for the entire temperature range of exchange broadening. The errors of the rate constants were estimated as described by Binsch and Kessler[14] for the non-iterative procedure.

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REFERENCES

[1]H. O. House, W. J. Campbell and M. Gall, *J. Org. Chem.* **35**, 1815 (1970).
[2]R. L. Clough and J. D. Roberts, *J. Am. Chem. Soc.* **98**, 1018 (1976).
[3]R. L. Clough and J. D. Roberts, *J. Org. Chem.* **43**, 1328 (1978).
[4]G. Binsch, personal communication.
[5]D. A. Kleier and G. Binsch, Program 165, Quantum Chemistry Program Exchange, Indiana University (1970).
[6]D. Höfner, D. S. Stephenson and G. Binsch, *J. Magn. Reson.* **32**, 131 (1978); and refs therein.
[7]D. S. Stephenson and G. Binsch, *Ibid* **32**, 145 (1978).
[8]D. Lauer and H. A. Staab, *Chem. Ber.* **102**, 1631 (1969).
[9]H. Brettschneider, Dissertation, Heidelberg, 1971.
[10]H. A. Staab, C. Krieger and Ching-sung Chi, in preparation.
[11]J. Almlöf, *Chem. Phys.* **6**, 135 (1974) and refs therein.
[12]H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.* **91**, 3517 (1969).
[13]H. A. Staab and Ching-sung Chi, in preparation.
[14]G. Binsch and H. Kessler, *Angew. Chem.* **92**, 445 (1980).