Conformational Studies by Dynamic NMR. 52.[1] Structure and Stereomutation of Conformational Enantiomers of 1,8-Diacylnaphthalenes

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Contrary to the symmetrically substituted 1,8-dibenzoylnaphthalenes the corresponding 1,8-diacylnaphthalenes were found to exist solely in the anti (racemic) conformation. The structure was assessed by ^{13}C (magic angle spinning) NMR spectroscopy as well as by X-ray diffraction in the solid and by differential NOE experiments in solution. The presence of prochiral substituents allowed to measure the degenerate enantiomerisation barrier by computer simulation of the ^1H NMR line shape as function of temperature. The barriers increased with the bulkiness of the alkyl substituents R bonded to the carbonyl moiety: they cover the range 6.7 kcal mol^{-1} (R = CH_2Me) to 9.0 kcal mol^{-1} (R = CH_2Ph). Molecular mechanics calculations suggest that the stereomutation is a stepwise rotational process with the R groups passing over the position 2 of the naphthalene ring.

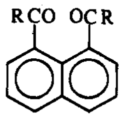
Introduction

Naphthalenes bonded to sp^2 carbons in positions 1,8 can originate rotational conformers owing to the restricted rotation about the substituent−naphthalene bond.[2−4] Due to the steric repulsions in the peri positions, the substituents adopt a conformation having the plane containing the sp^2 carbons twisted with respect to the plane of naphthalene. When the two 1,8 substituents are equal and do not bear a local 2-fold symmetry axis syn (meso) or anti (racemic) conformers can be, in principle, observed.[3,4] This happened, for instance, in a few substituted 1,8-dibenzoylnaphthalenes, where both conformers (having the C═O moieties parallel or antiparallel) were detected by NMR spectroscopy.[3] The barrier required to interconvert one such a conformer into the other could thus be measured[3] by line shape analysis of the temperature-dependent NMR signals. On the other hand, there are not analogous investigations available for the corresponding RC═O derivatives, where R is an aliphatic rather than an aromatic group.

By using molecular mechanics calculations[5] we found that in the case of such RC═O substituents only one of the two conformers (specifically the anti) is expected to be populated at the equilibrium, whereas the other one (syn) is predicted to have an energy too high to be experimentally detectable. As a consequence the multiplicity of the NMR signals is not expected to change when the naphthalene−carbonyl bond rotation is "locked" at low temperature, unless a prochiral probe[6] is present in the molecule. In order to investigate the stereomutation of 1,8-diacylnaphthalenes, a number of derivatives, having prochiral R groups in the RC═O substituents, were thus synthesized.

Results and Discussion

Compounds **1-6** were investigated by variable-temperature NMR spectroscopy: with the obvious exception of **1** (R = Me), all the R groups displayed anisochronous hydrogens in the proton spectra at appropriate low temperatures.



R = Me **1**
= CH_2Me **2**
= CH_2Et **3**
= CH_2Pr^i **4**
= $CHMe_2$ **5**
= CH_2Ph **6**

The restricted rotation about the naphthalene−carbonyl bond renders in fact diastereotopic the geminal substituents, such as the hydrogens of the α-methylene groups (in **2**, **3**, **4**, **6**) or the isopropyl methyl groups (in **5**). An example is reported in Figure 1 where the CH_2 proton signal (decoupled at the frequency of the methyl group) is displayed at various temperatures. The decoupling reduces the CH_2 quartet to a singlet which splits

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[4] (a) House,H. O.; Campbell,W. J.; Gall, M. *J. Org. Chem.* **1970**, *35*, 1585. (b) Clough, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1018. (c) Cozzi, F.; Cinquini, M.; Annunziata, R.; Dwyer, T.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 5729.

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[6] (a) Mislow, K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1. (b) Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307.

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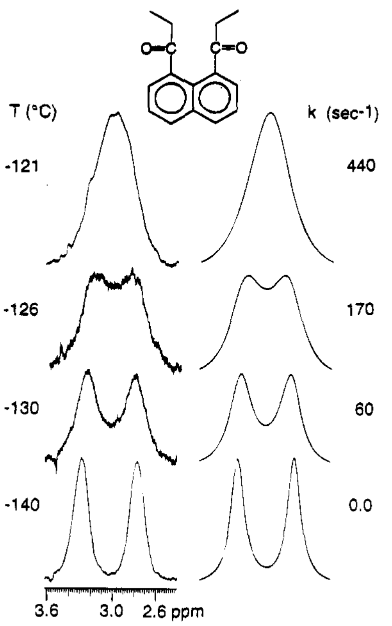

Figure 1. Temperature dependence (left) of the CH_2 hydrogen signals of **2** (300 MHz in CHF_2Cl/CD_2Cl_2). The spectra were obtained by decoupling at the frequency of the CH_3 triplet. The computer simulations (right) were obtained with the rate constants (k, s^{-1}) indicated.

Table 1. Free Energies of Activation (ΔG^* in kcal mol^{-1}) for the Stereomutation of Derivatives 2–6. The Chemical Shift Differences ($\Delta\nu$, at 200 MHz) of the Anisochronous Methylene Protons Are Reported at the Temperature (in °C) of Detection

compd	ΔG^*	$\Delta\nu$ (Hz)	solvent
2 (R = CH_2Me)	6.7 ± 0.2	152 (−140)[a]	CHF_2Cl/CD_2Cl_2
3 (R = CH_2Et)	7.6 ± 0.15	95 (−118)	CHF_2Cl/CD_2Cl_2
4 (R = CH_2Pr^i)	7.8 ± 0.15	137 (−115)	CHF_2Cl/CD_2Cl_2
5 (R = $CHMe_2$)	8.4 ± 0.15	35 (−110)[b]	CHF_2Cl/CD_2Cl_2
6 (R = CH_2Ph)	9.0 ± 0.15	150 (−95)	CD_2Cl_2

[a] At 300 MHz. [b] Signals of the methyl groups.

into a pair of equally intense signals at −140 °C (the expected geminal coupling is obscured by the broad line width due to the viscosity at such a low temperature). The ΔG^* value obtained[7] from the computer line shape analysis is reported in Table 1 together with those of **3-6**.

As predicted by MM calculations both the ^1H and ^{13}C spectra of **2** reveal the presence of only one of the two possible conformers at low temperature. All the other derivatives (**3-6**) also display an analogous spectral behavior, indicating that in each case only a single conformer is appreciably populated. Although according to the calculations the conformer with the CO moieties in the anti relationship (racemic) is expected to be the more stable, experimental proofs are obviously required for an unambiguous assignement.

A first indication concerning the preferred conformation could be rapidly obtained by means of high-resolution ^{13}C (cross polarization−magic angle spinning) spectra in the solid state. Two enantiotopic carbons that are not related by a plane or a center of symmetry usually display, in the solid, a pair of equally intense ^{13}C lines.[8]

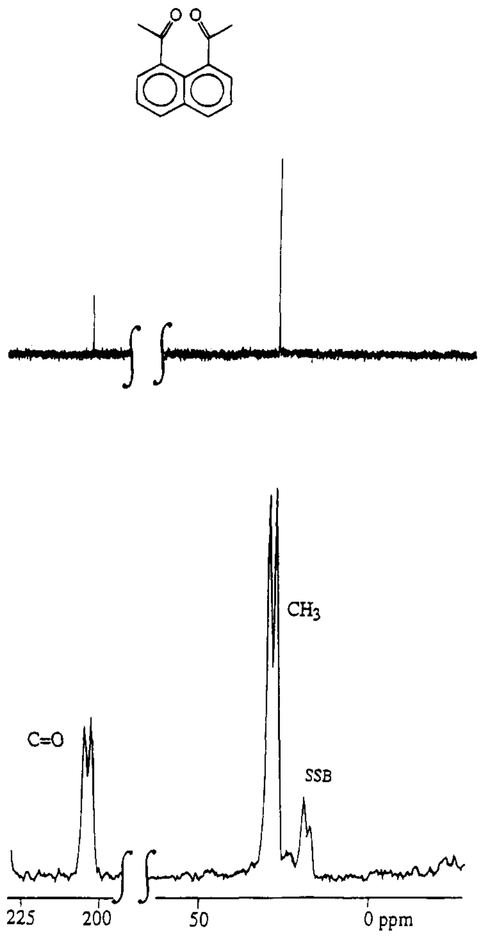

Figure 2. Methyl and carbonyl ^{13}C signals of **1** (R = Me) in a $CDCl_3$ solution (top) and in the solid state (bottom). The lines marked SSB are spinning side bands.

Accordingly, the meso form, which possesses a plane of symmetry, should yield in the solid a spectrum with the same multiplicity as in solution; the racemic conformer, on the contrary, should have the lines of the solution spectrum split into pairs in the solid. In the case of **2** two lines were actually observed for the CO and CH_3 carbons while the line of CH_2 was too broad to be resolved, indicating a near degeneracy.[9] An analogous splitting was also detected for the signals of **4**, suggesting that the single conformer observed at low temperature was indeed the same (racemic) for all the compounds. The solid-state NMR also allowed us to investigate the conformation of **1**, where the absence of prochiral probes had prevented the monitoring of the dynamic process in solution. As shown in Figure 2 the single lines observed in solution for the CO and CH_3 carbons of **1** are split into pairs in the solid state. As no additional lines, corresponding to a second conformer, were observed, compound **1** also must exist as a single (racemic) conformer.

Although quite useful for obtaining rapid information upon the conformational arrangement, the solid-state NMR approach is not completely unambiguous. A symmetric meso structure might also display, in principle, a splitting of the signals: this would occur if the elements

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(7) The ΔG^* values were calculated assuming a coefficient transmission of 1/2 because of the proposed mechanism for the interconversion (see Figure 5). The use of an unitary transmission coefficient would enhance the values by 0.2 kcal mol^{-1}. Within the errors the ΔG^* values were found independent of the temperature (i.e., $\Delta S^* = 0$) as often observed in conformational processes. Accordingly, the ΔG^* values can be meaningfully compared even if obtained at different temperatures.

(8) (a) Hill, H. D. W.; Zens, A. P.; Jacobus, J. *J. Am. Chem. Soc.* **1979**, 101, 7090. (b) Casarini, D.; Lunazzi, L.; Macciantelli, D. *J. Org. Chem.* **1988**, *53*, 177.

(9) The lines of the aromatic region were too broad to be properly analyzed owing to the large contribution of the chemical shift anisotropy.

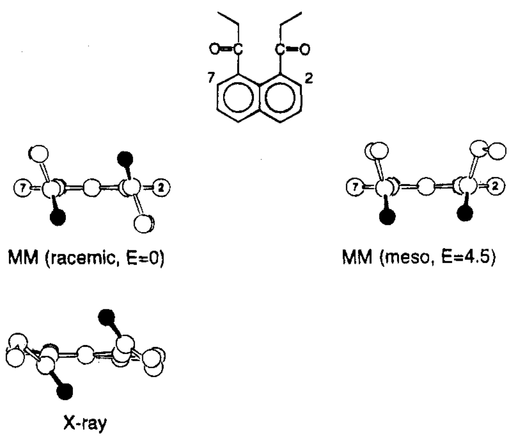

Figure 3. Top view of the anti (racemic) and syn (meso) conformers of **2** as obtained from MM calculations (top): the relative computed energies (*E* in kcal mol^{-1}) are also indicated. Underneath is displayed the X-ray structure. The carbonyl moiety is indicated in black for convenience.

of symmetry of the molecule are not coincident with those of the crystal (site symmetry lower than molecular symmetry).[8,10] Although it seems unlikely that this would occur for each of the three compounds (**1**, **2**, **4**) investigated by solid-state NMR, the support of an X-ray diffraction determination was sought in the case of **2**. In Figure 3 its crystal structure is reported and compared with the results of the MM calculations. No doubt is left that the molecule adopts an anti (racemic) conformation.

Naphthalenes bearing bulky 1,8 substituents have been reported to display a noticeable deformation of the ring framework,[11] the corresponding flipping barrier having also been determined.[12] In **2** a moderate distortion was indeeed observed in that the plane defined by C1, C9, C8 is twisted by 5.3° with respect to that of C4, C10, C5; this forces the carbonyl carbons bonded to C1 and C8 to lie, respectively, 0.40 ± 0.03 Å above and below the mean plane of naphthalene.

A comparison of the computed and experimental anti structures of Figure 3 also shows that the torsion angles of the CO moiety with respect to the mean plane of naphthalene are quite different (73° and 42°, respectively), the oxygen atoms pointing inward, in both cases, toward position 9.[13] This difference could be a consequence of the approximations of the MM method but might, alternatively, reflect a real modification of the geometry in a condensed phase with respect to the isolated molecule. In order to have an indication concerning the torsion angle adopted in solution, a differential nuclear Overhauser enhancement (NOE) experiment[14] was thus performed.

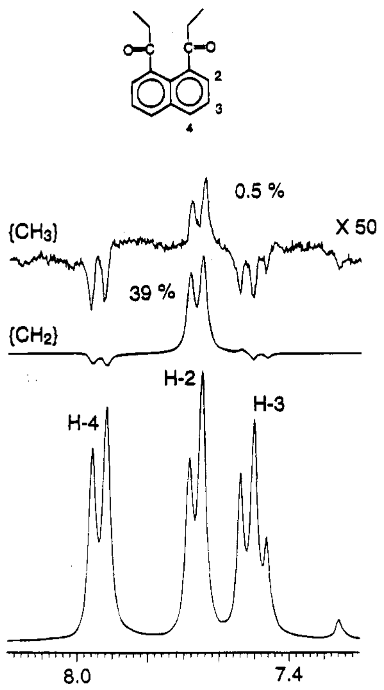

Figure 4. Differential NOE spectra of the aromatic region of **2**. Lower trace: control spectrum. Middle trace: NOE due to the irradiation of the CH_2 quartet. Upper trace: NOE due to the irradiation of the CH_3 triplet (this scale has been vertically amplified by a factor of 50). The signals of H-2 display positive NOE (39% and 0.5% as indicated) whereas those of H-3 and H-4 display negative effects.

Irradiation of the multiplets of the CH_2 or CH_3 groups enhanced the H-2 signal of the aromatic region, as shown in Figure 4 (the H-3 and H-4 signals displayed a negative NOE effect). Because of the different interproton distances, the NOE obtained by irradiating the CH_2 quartet is much larger (39%) than that obtained by irradiating the CH_3 triplet (0.5%). The experimental errors were estimated not to exceed 10% of the observed values. In a first approximation the NOE effect increases proportionally with the number of irradiated protons when, as in the present case, the observed protons relax through mechanisms that do not involve the protons being irradiated (H-2 essentially relaxes through the coupling with the other ring hydrogens).[14,15] Also, the NOE values are approximately dependent upon the 6th power of the reciprocal interproton distances.[14,15] Thus, if the average distances between H-2 and the CH_2 or the CH_3 hydrogens are, respectively, indicated as $r^{(\mathrm{CH_2})}$ and $r^{(\mathrm{CH_3})}$, the following relationship is obtained:

$$[(39/2)/(0.5/3)]^{1/6} = r^{(\mathrm{CH_3})}/r^{(\mathrm{CH_2})} = 2.2$$

The averaged distances *r*, derived[16] from the MM calculations (4.88 and 3.25 Å for CH_3 and CH_2, respectively) are

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[10] Lyerla, J. R.; Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 208.

[11] (a) Blount, J. F.; Cozzi, F.; Danewood, J. R.; Iroff, D. L.; Siøstrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 99. (b) Ashton, P. R.; Brown, G. R.; Foubister, A. J.; Smith, D. R.; Spencer, N.; Stoddart, F. J.; Williams, D. J. *Tetrahedron Lett.* **1994**, *34*, 8333 and references cited therein.

[12] (a) Alder, R. W.; Anderson, J. E. *J. Chem. Soc., Perkin Trans. 2* **1973**, 2086. (b) Anderson, J. E.; Franck, R. W. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1581.

[13] It is noteworthy that the MM calculations predict no appreciable distortion for the naphthalene ring in the minimum energy conformation having the naphthalene–carbonyl torsion angles equal to 73°. The same calculations, however, predict a ring distortion of 7° if the torsion angle is forced to be 42° as in the X-ray structure: a value which compares favorably with the experiment (5.3°). Obviously, the distortion from planarity of the naphthalene ring is a function of the torsion angle, i.e., of the mutual steric repulsion of the two peri substituents. Accordingly, in the rotational transition state (see further in the text) the computed ring distortion has increased to 11° since the steric strain between the two substituents has become even larger.

[14] Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, VCH Publishers, Inc.: New York, 1989.

[15] (a) Davalli, S.; Lunazzi, L.; Macciantelli, D. *J. Org. Chem.* **1991**, *56*, 1739. (b) Casarini, D.; Lunazzi, L.; Macciantelli, D. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1363. (c) Casarini,D.; Lunazzi, L.; Pasquali, F.; Gasparrini, F.; Villani, C. *J. Am. Chem. Soc.* **1992**, *114*, 6521. (d) Casarini,D.; Foresti, E.; Gasparrini, F.; Lunazzi, L.; Macciantelli, D.; Misiti, D.; Villani, C. *J. Org. Chem.* **1993**, *58*, 5674.

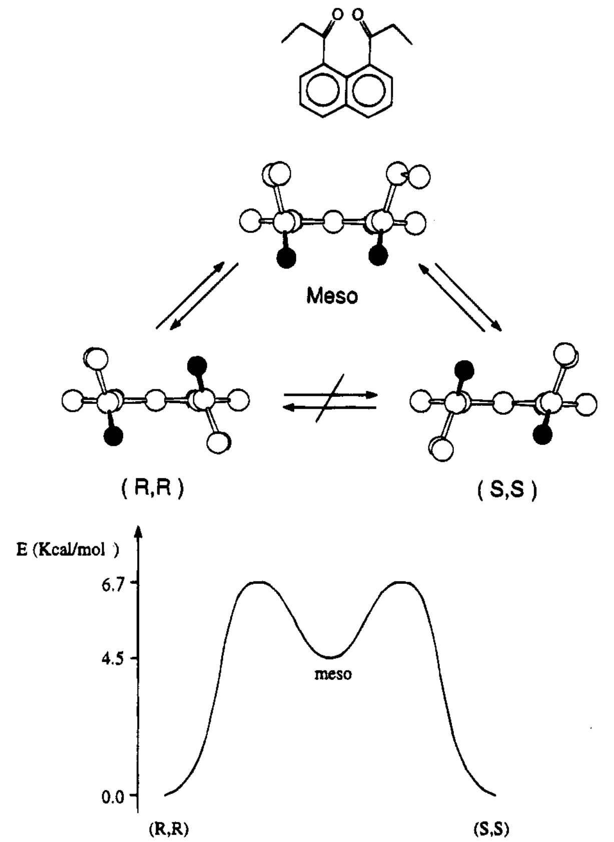

Figure 5. Diagram representing the stereomutation process which transforms the *RR* into the *SS* conformational enantiomer of **2** *via* the meso form. The energy of the latter (4.5 kcal mol^{-1}) is the result of MM calculations and that of the transition state (6.7 kcal mol^{-1}) is the experimental value (the corresponding computed value would be 10.1 kcal mol^{-1}). The synchronous rotation of both carbonyls, which would directly interconvert *RR* into *SS*, is believed not to occur (see text).

obviously larger than those derived from the X-ray structure (4.75 and 2.55 Å, respectively) since they correspond to a larger torsion angle (73° vs 42°). The ratios of such distances in the two cases are, respectively, 1.5 and 1.9, the latter value being almost equal, within the errors, to that derived from the NOE experiments (i.e., 2.2). This suggests that the naphthalene–carbonyl torsion angle should be, in solution, very similar to the one measured in the solid state.

Having established that only the conformers with the carbonyl groups in the anti relationship are appreciably populated, the stereomutation observed for **2-6** should be described as the rotation of one carbonyl group which transforms the *RR* enantiomer into the meso conformer, followed by a rotation of the second carbonyl group which would subsequently yield the *SS* enantiomer, as shown in Figure 5. Although the meso form corresponds to a minimum in the stereomutation pathway, it cannot be experimentally detected as the corresponding energy level is computed to be 4.5 kcal mol^{-1} higher than the energy of the racemic ground state. At −140 °C such a value entails a population ratio at the equilibrium as low as 25×10^{-6}:1.

The rotation of the RCO group might lead either to a transition state with the CO moiety passing over the hydrogen in position 2 of the naphthalene ring or, alternatively, to a transition state where the R group passes over H-2. As no experiment can discriminate between these two situations, the choice had to be made on the basis of the calculations: in derivative **2** the barrier for CO passing over H-2 (16.2 kcal mol^{-1}) is substantially higher than for the ethyl group passing over H-2 (10.1 kcal mol^{-1}). The latter value not only is lower but is also much closer to the measured barrier (6.7 kcal mol^{-1}), thus suggesting that the enantiomerization process most likely occurs through this second pathway. The simultaneous rotation of both the carbonyl groups might also interconvert, in principle, the *RR* into the *SS* enantiomer, without passing through the meso conformer. Such a concerted motion would require a symmetrical transition state, with the two oxygen atoms pointing toward C9 and lying on a plane approximately coincident with that of the naphthalene ring. The MM calculations predicted, however, that in this event the barrier would be much higher than for the stepwise process (16.7 rather than 10.1 kcal mol^{-1}).

The experimental ΔG^* values of Table 1 increase regularly along the series **2-5**, clearly reflecting the increasing steric hindrance of the R substituents. The barrier for **6** (R = CH_2Ph), which is slightly higher than that of **5** (R = $CHMe_2$), is somehow surprising in that the isopropyl group is expected to be bulkier than the benzyl group. In the present case, however, the MM calculations indicate that the preferred anti conformer of **6** has the two phenyl rings staying in parallel planes facing each other above the plane of the naphthalene. The corresponding rotational transition state computed for the CH_2Ph group passing over H-2 has a relative energy of 11.0 kcal mol^{-1}: the same calculations indicate for **5** an almost equal energy (10.9 kcal mol^{-1}). Accordingly, owing to the mutual interactions of the two phenyl rings, it is conceivable to predict a rotational barrier for **6** certainly not lower than for **5**, thus accounting for the trend of the corresponding experimental values of Table 1 (i.e., 9.0 and 8.4 kcal mol^{-1} for **6** and **5**, respectively).

Experimental Section

Materials. Compounds **1-6** were prepared according to the general procedure of the literature.[17,18] Compound **1** has been reported,[18] whereas **2**, although prepared,[2a] has not been described. The analytical data for **2-6** are as follows.

1-(8-Propionylnaphthalen-1-yl)propan-1-one (2): mp 133–135 °C; ^1H NMR ($CDCl_3$) δ 1.24 (6H, t, J = 7.5 Hz, CH_3), 3.10 (4H, q, J = 7.5 Hz, CH_2), 7.50 (2H, dd, H-3, H-6), 7.67 (2H, dd, H-2, H-7), 7.95 (2H, dd, H4, H-5); ^{13}C NMR ($CDCl_3$) δ 8.1 (CH_3), 35.0 (CH_2), 125.3 (CH, Ar), 126.6 (CH, Ar), 131.7 (CH, Ar), 126.1 (C, Ar), 135.1 (C, Ar), 139.4 (C, Ar), 207.9 (CO). Anal. Calcd for $C_{16}H_{16}O_2$: C 79.97; H, 6.71. Found: C, 79.91; H, 6.75.

1-(8-Butyrylnaphthalen-1-yl)butan-1-one (3): mp 136–137 °C; ^1H NMR δ ($CDCl_3$) 1.06 (6H, t, J = 7.4 Hz, CH_3), 1.80 (4H, m, β CH_2), 3.05 (4H, 7, J = 7.4 Hz, α CH_2), 7.50 (2H, dd, H-3, H-6), 7.70 (2H, dd, H-2, H-7), 7.94 (2H, dd, H-4, H-5); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3), 17.5 (β CH_2), 44.0 (α CH_2), 125.4 (CH, Ar), 127.1 (CH, Ar), 132.0 (CH, Ar), 126.3 (C, Ar), 135.3 (C, Ar), 139.8 (C, Ar), 207.0 (CO). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.62; H, 7.48.

3-Methyl-1-[8-(3-methylbutyryl)naphthalen-1-yl]butan-1-one (4): mp 144–146 °C; ^1H NMR ($CDCl_3$) δ 1.07 (12H, d, J

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[16] As the NOE values depend upon the sixth power of the reciprocal distances, the average was calculated as $r = (\sum r_i^6/n)^{1/6}$ where r_i is the individual distance between a pair of hydrogens and n is the number of distances entering into the average (thus, n = 2 for CH_2 and n = 3 for CH_3).

[17] Maxim, N. *Bull. Soc. Chim. Fr.* **1928**, *43*, 769; **1929**, *45*, 1137.

[18] Stille, J. K.; Foster, R. T. *J. Org. Chem.* **1963**, *28*, 2703.

= 6.6 Hz, CH_3), 2.35 (2H, m, CH), 2.95 (4H, d, J = 6.7 Hz, CH_2), 7.25 (2H, dd, H-3, H-6), 7.71 (2H, dd, H-2, H-7), 7.94 (2H, dd, H-4, H-5); ^{13}C NMR δ ($CDCl_3$) 23.0 (CH_3), 24.2 (CH), 50.6 (CH_2), 125.5 (CH, Ar), 127.3 (CH, Ar), 132.1 (CH, Ar), 126.5 (C, Ar), 135.5 (C, Ar), 140.2 (C, Ar), 206.3 (CO). Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.10; H, 8.20.

1-(8-Isobutyrylnaphthalen-1-yl)-2-methylpropan-1-one (5): ^1H NMR ($CDCl_3$) δ 1.37 (12H, d, J = 6.9 Hz, CH_3), 3.39 (2H, sept, J = 6.9 Hz, CH), 7.51 (2H, dd, H-3, H-6), 7.78 (2H, dd, H-2, H-7), 7.95 (2H, dd, H-4, H-5); ^{13}C NMR ($CDCl_3$) δ 18.8 (CH_3), 38.7 (CH), 125.3 (CH, Ar), 127.7 (CH, Ar), 132.4 (CH, Ar), 127.4 (C, Ar), 135.8 (C, Ar), 138.6 (C, Ar), 209.3 (CO). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.49; H, 7.55.

2-Phenyl-1-[8-(phenylacetyl)naphthalene-1-yl]ethanone (6): mp 138–141 °C; ^1H NMR ($CDCl_3$) δ 4.37 (4H, s, CH_2), 7.15–7.45 (10H, m, Ph), 7.56 (2H, dd, H-3, H-6), 7.85 (2H, dd, H-2, H-7), 8.00 (2H, dd, H-4, H-5); ^{13}C ($CDCl_3$) δ 48.4 (CH_2), 125.1 (CH, Ar), 126.7 (CH, Ar), 127.0 (CH, Ar), 128.4 (CH, Ar), 130.3 (CH, Ar), 131.9 (CH, Ar), 134.2 (C, Ar), 134.9 (C, Ar), 138.7 (C, Ar), 203.6 (CO). Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.61; H, 4.82.

X-ray Diffraction. The crystal system of **2** is monoclinic with space group $P2_1/c$, a = 9.728(4) Å, b = 8.469(4) Å, c = 16.734(5) Å, β = 104.98(5)°, V = 1331.8 Å^3, Z = 4, D_c = 1.20 g cm^{-3}. Mo Kα radiation = 0.7107 Å, μ (Mo Kα) = 0.43 cm^{-1}, $F(000)$ = 512.0. Intensity data were collected by a CAD4 diffractometer using $\omega/2\theta$ scan range 2.5° $\le \theta \le$ 25°. The unit cell parameters were determined by a least squares refinement on diffractometric angles for 25 automatically centered reflections 8° $\le \theta \le$ 14°. Of 1888 independent reflections, 829 having $I < 2.6\sigma(I)$ were considered unobserved. The final agreement index was R = 0.053, S = 0.90. Maximum Δ/σ = 0.020. Final difference Fourier map excursion 0.16 to −0.13 e Å^{-3}. A listing of fractional atomic coordinates, thermal parameters, relevant atomic distances and angles for **2** have been deposited at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

NMR Measurements. The variable temperature NMR spectra in solution were recorded either at 200 or 300 MHz (Gemini, Varian): the temperature within the probe was calibrated as described in ref 19. The computer simulations of the line shape were performed with a two-sites program[19] based on the Bloch equations, and the best fit was visually judged by superimposing the plotted and experimental traces. The samples were prepared by connecting the NMR tubes, containing a CD_2Cl_2 solution of the compounds, to a vacuum line and condensing the gaseous CHF_2Cl (the latter being approximately 3:1 v/v) with liquid nitrogen. The tubes were then sealed *in vacuo* and introduced in the precooled probe of the spectrometer. The differential NOE measurements were carried out in $CDCl_3$ solutions (previously purged from dissolved oxygen using a nitrogen stream) by presaturating the signals for about 10 s and acquiring the spectra with the decoupler turned off. The various lines of the multiplets were saturated by cycling the irradiation frequencies about 50 times. A program that accumulates the difference between the two FID's (that being irradiated and that acquired with the irradiation frequency kept away from any signal) was employed. Usually 1000 scans were accumulated at constant temperature (21 °C) and transformed with a line broadening of 2–3 Hz. The control spectrum was subsequently acquired with half the number of scans. The solid-state ^{13}C CP MAS spectra were obtained at 75.48 MHz (Bruker, CXP). The powder was fitted in a ZrO_2 rotor spun at 3.5 KHz and the spectra acquired with a standard cross polarization sequence using a contact time of 5 ms and a recycling time of 3 s.

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