

## Naphthoyl $\sigma$ -Radicals: Elucidation of their Conformational Behaviour by Electron Spin Resonance

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The relative conformer stability in a series of naphthoyl  $\sigma$ -radicals has been investigated by e.s.r. techniques over a wide temperature range. In the case of the 1-naphthoyl radical two rotamers, with a conformational ratio apparently different from that of the parent molecule, were detected. In contrast, in the 2-naphthoyl radical the relative amounts of the conformers are, most likely, dependent upon those in the precursor aldehyde. Structural assignments were achieved by comparing the experimental data with INDO h.f.s. constants. The steric effect on the ratio of the conformers caused by methyl substituents was also examined in order to ascertain the reliability of the INDO approximation.

The relationships amongst conformation, stability, and e.s.r. spectra for aliphatic acyl  $\sigma$ -radicals ( $R\dot{C}O$ ) have been thoroughly investigated during the last few years.<sup>1-4</sup> In contrast, there have been very few studies on aromatic acyl  $\sigma$ -radicals ( $Ar\dot{C}O$ ). Previous papers were concerned with kinetic investigations<sup>5-8</sup> as well as with the conformational properties of the aromatic acyl radicals derived from benzene-, thiophene-, furan- and pyrrole-carbaldehydes.<sup>7,9</sup> In particular, it has been shown that the conformer ratio of the radicals is either independent of or dependent on that of the parent molecules according to the value of the rotational barrier in the radical. Recently, we have found a parallel behaviour between the rotational barrier in benzoyl  $\sigma$ -radicals and that in the corresponding parent molecules.<sup>10</sup> We report here an e.s.r. study on 1- and 2-naphthoyl  $\sigma$ -radicals and some of their derivatives, with the particular aim of comparing their conformational behaviour with that of the parent aldehydes previously investigated by n.m.r. and theoretical approaches.

### Results and Discussion

Naphthoyl  $\sigma$ -radicals were generated by photolysis of di-*t*-butyl peroxide ( $Bu^tOOBu^t$ ) in the presence of the corresponding aldehydes in cyclopropane at low temperature. The radicals detected, and their e.s.r. parameters, are listed in the Table.

The assignment of the hyperfine splitting (h.f.s.) constants and the preferred conformation are justified in the following analysis.

**1-Naphthoyl Radicals.**—Photolysis of di-*t*-butyl peroxide in the presence of 1-naphthaldehyde in cyclopropane below 183 K produced the spectra of two radicals, one consisting of a triplet,  $\dagger$   $a(2H)$  1.2 G, and the other a doublet,  $a(H)$  1.45 G, with a smaller further hyperfine splitting  $a(H)$  0.35 G (Figure 1). Within experimental error (*ca.*  $\pm 5\%$ ), the relative concentration of the two radicals was 55:45. The low  $g$  factor unambiguously identifies the radicals as  $\sigma$ -acyl radicals.

The existence of two rotational planar conformers (*Z* and *E*) in 1-naphthaldehyde is well documented from n.m.r. experiments:<sup>11-15</sup> the low-temperature n.m.r. measurements indicate that the *Z*-conformer is the more stable (90% from dynamic n.m.r. measurements;<sup>13</sup> 77% from the lanthanide-induced shift method)<sup>14</sup> and the two conformations are separated by an

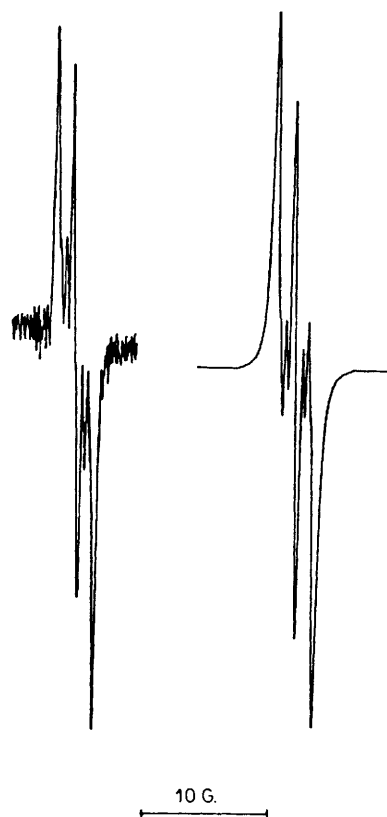


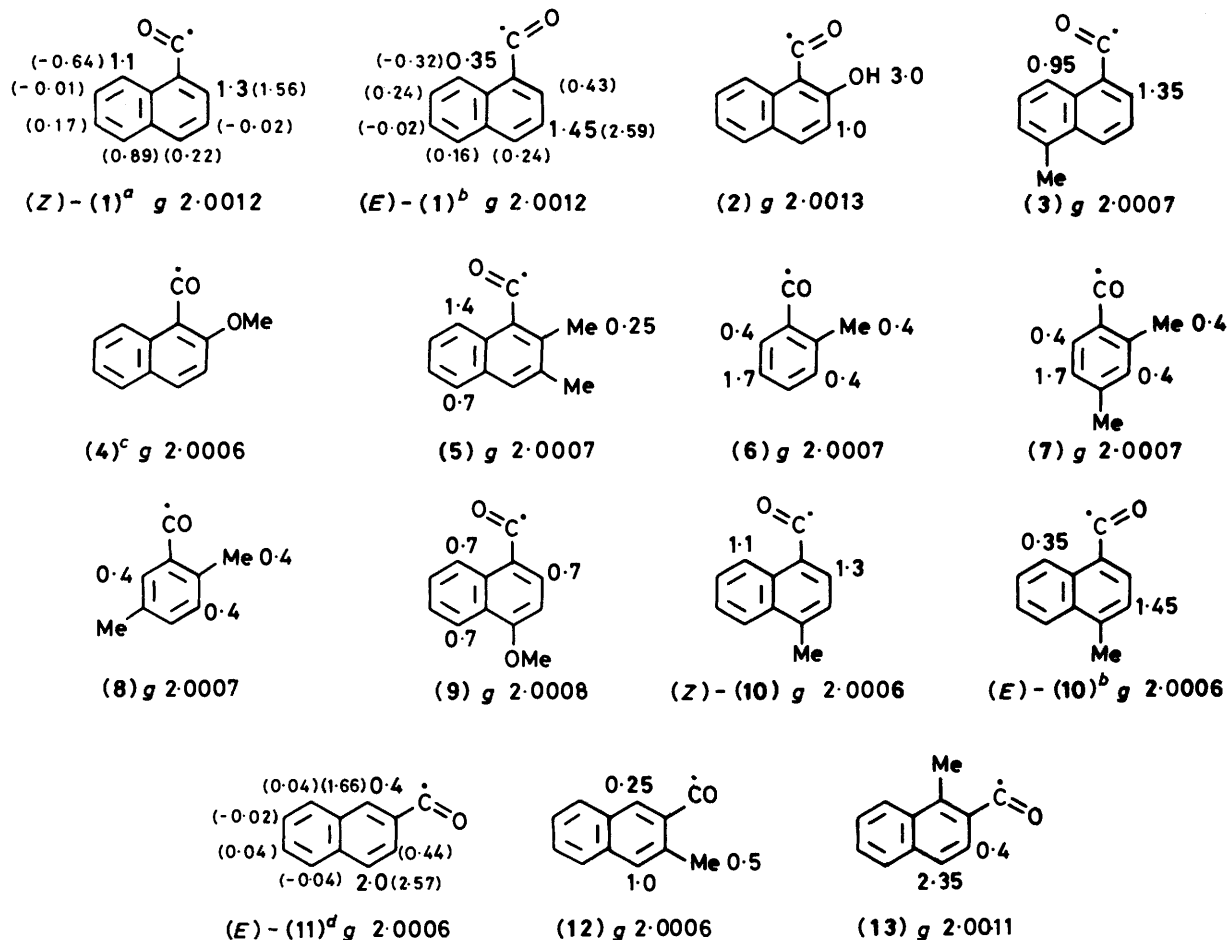
Figure 1. Experimental (left) and computer-simulated (right) spectra of the 1-naphthoyl radical at 148 K; the simulated spectrum was obtained with a *Z*:*E* conformer ratio of 55:45

appreciable rotational barrier ( $6.4 \text{ kcal mol}^{-1}$ ).<sup>13</sup>  $\ddagger$  The conformer ratio (55:45) in the 1-naphthoyl radical (**1**) is apparently different from that in the parent molecule, indicating that the radical conformers reach their own thermodynamic equilibrium. In fact, it has been previously suggested<sup>7</sup> that aromatic acyl radicals whose parent aldehydes have rotational barriers lower than about  $9 \text{ kcal mol}^{-1}$  interconvert faster than they decay.

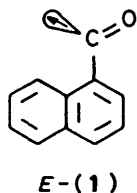
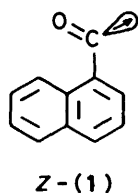
The assignment of the experimental h.f.s. constants to similar amounts of *Z*- and *E*-conformers was based on INDO calculations and experimental proof (Table).

$\dagger$  The triplet is due to near degeneracy of two non-equivalent hydrogen atoms in the naphthalene ring; the best agreement between experimental and simulated e.s.r. spectra is obtained by taking into account two different hyperfine splittings,  $a(H)$  1.1 and 1.3 G.

$\ddagger$  1 kcal = 4.184 kJ.

**Table.** Experimental and INDO (in parentheses) h.f.s. constants (G) of the radicals (1)–(13)

<sup>a</sup> INDO (in parentheses) h.f.s. constants (G) for a twisted ( $\theta$  10°) conformation; for a planar conformation;  $a(\text{H-2})$  1.77,  $a(\text{H-3})$  -0.15,  $a(\text{H-4})$  0.41,  $a(\text{H-5})$  1.04,  $a(\text{H-6})$  0.12,  $a(\text{H-7})$  0.09,  $a(\text{H-8})$  -1.04 G. <sup>b</sup> The experimental coupling (0.35 G) can be assigned to the proton at position 8 or 2. <sup>c</sup> Peak-to-peak separation 1.0 G. <sup>d</sup> INDO h.f.s. constants of the Z-conformation:  $a(\text{H-1})$  0.32,  $a(\text{H-3})$  1.68,  $a(\text{H-4})$  -0.11,  $a(\text{H-5})$  -0.04,  $a(\text{H-6})$  0.04,  $a(\text{H-7})$  0.20,  $a(\text{H-8})$  0.05 G.



For the *E*-conformer, INDO calculations performed on a planar arrangement predict only one relatively large h.f.s. constant, at position 3 in agreement with the *W*-empirical rule. This suggests that the largest h.f. s. in  $\sigma$ -radicals is at the position corresponding to the extreme of a zig-zag chain of bonds, having the orbital of the unpaired electron at the other extreme.<sup>16</sup> Therefore, the doublet of doublets,  $a(\text{H})$  1.45 and 0.35 G, observed at low temperature, was attributed to the *E*-conformation of the 1-naphthoyl radical.

These conclusions are not in disagreement with the e.s.r. parameters of the 2-hydroxy-1-naphthoyl radical (2),  $a(\text{H})$  1.0 and 3.0 G, which could have essentially the same *E*-structure as found for the parent molecule,<sup>12,14,15</sup> because of a strong internal OH...O hydrogen bond.

The smaller  $a(\text{H})$  value has been assigned to the proton at position 3 and the larger to the OH hydrogen. This follows from a deuterium-labelling experiment carried out on 2-hydroxy-1-naphthaldehyde. The OH hydrogen of this derivative was replaced by deuterium and the spectrum of the corresponding radical was observed. The disappearance of the larger  $a(\text{H})$  splitting, which was reduced by a factor of 6.5, indicates that in (2) the OH hydrogen is responsible for the larger coupling. The asymmetry of the spectral lines of the radical (2) and its deuterated derivative indicates that the *Z*-structure is also present; however, we were unable to give a precise estimate of its h.f.s. constants. To support our findings, 8-methyl-1-naphthaldehyde was prepared. Since the conformational ratio is strongly dependent on the substituent, we would expect in this case the *E*-conformer to be more populated. Unfortunately, however, no e.s.r. spectrum was detected under our experimental conditions. For the *Z*-conformer INDO calculations were performed taking into account a planar and a twisted arrangement obtained by rotating the carbonyl group around the Ar-CO bond through an angle  $\theta = 10^\circ$  (Table). In fact, as reported for the parent aldehyde,<sup>13,14</sup> a steric effect due to the presence of the *peri*-hydrogen atom might cause such a non-planar conform-

ation. For both the *Z*-models examined, calculations predict three relatively large h.f.s. constants at positions 2, 5, and 8.

However, since we observed only two quite large couplings, we thought that more experimental proof was necessary in order to establish their assignment. When the hydrogen at position 5 is replaced by a methyl group, the e.s.r. spectrum, at 188 K, shows that two protons with quite large h.f.s. constants,  $a(\text{H})$  0.95 and 1.35 G, are still present. Accordingly, we were able to assign the observed couplings to positions 2 and 8 of the *Z*-conformer.

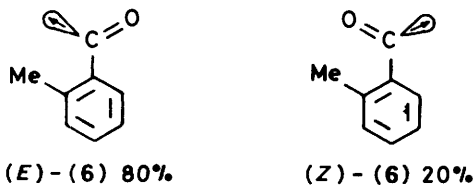
No e.s.r. evidence for the *E*-conformer is apparent from the spectrum of the 5-methyl-1-naphthoyl radical (3) in cyclopropane solution: most likely in this case its lines are beneath those of the *Z*-conformer. In fact, when a mixture of cyclopropane and benzene (80:20) is employed as solvent, the h.f.s. constants due to the two radical conformers are slightly shifted, and an asymmetric e.s.r. spectrum is detected.

Above *ca.* 183 K the radicals from 1-naphthaldehyde decay under our experimental conditions, preventing us from observing their dynamic behaviour. The barrier to internal rotation for the *Z*-to-*E* exchange in 1-naphthaldehyde<sup>13</sup> ( $\Delta G^\ddagger$  6.4 kcal mol<sup>-1</sup>) is lower than that in benzaldehyde<sup>17,18</sup> ( $\Delta G^\ddagger$  7.7 kcal mol<sup>-1</sup>). Since we have recently found<sup>10</sup> that the energy barrier in the benzoyl  $\sigma$ -radical is 2.8 kcal mol<sup>-1</sup>, we would expect, by analogy, a lower value in the 1-naphthoyl radical. However, the absence of line broadening effects at 183 K suggests that the rotational barrier about the C-CO bond is greater than 4.7 kcal mol<sup>-1</sup>.

Most likely a stabilizing effect on the ground state of (1) derives from a hydrogen-bond-type interaction of the carbonyl group with the *peri*-hydrogen\* as observed in the corresponding parent molecule,<sup>11,14</sup> and from interaction of the  $sp^2$  orbital containing the unpaired electron with the C-H *peri*-electron bond.

The 2-methoxy-1-naphthoyl radical (4) showed a spectrum consisting of a single broad line (peak-to-peak difference 1.0 G) throughout the temperature range used. With no information from proton coupling constants, the conformation of the radical cannot be assigned.

The 2,3-dimethyl-1-naphthoyl radical (5) displayed symmetric lines over the temperature range 143–173 K, thus indicating that it exists essentially as a single conformer. The carbonyl group is probably forced exclusively into the *Z*-conformation owing to steric hindrance by the methyl group at position 2. Such a change of the relative conformer populations was also observed when an *ortho*-hydrogen in the benzoyl radical was replaced by a methyl group, in (6).



In this case rotation about the C-CO bond is faster than in the unsubstituted benzoyl radical:<sup>9,10</sup> at 153 K a time-averaged spectrum is observed.† However, the *meta* h.f.s. constants

\* The interaction is evident from the magnitude of the coupling at position 8.

† This is consistent with a rotational model involving a planar ground state and a transition state with the CO  $sp^2$  orbital plane twisted by  $\pi/2$  with respect to the benzene ring. Whereas the twisted transition state should be almost unaffected by the introduction of a methyl group, the ground state should be destabilized as in the corresponding parent molecule.<sup>19</sup>

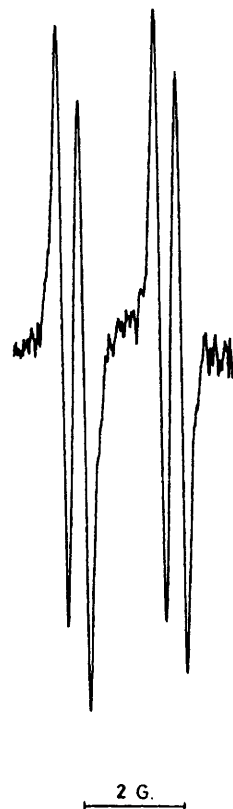


Figure 2. The e.s.r. spectrum of the 2-naphthoyl radical at 148 K

(Table), assigned on the basis of data for the 2,4-dimethyl- and 2,5-dimethyl-benzoyl radicals (7) and (8), allowed us to estimate the conformational ratio [(*E*)-(6) 80%; (*Z*)-(6) 20%]. In fact, as previously observed,<sup>10</sup> the total splitting of the *meta*-hydrogens in the benzoyl radical (2.2 G) seems to be almost unaffected by the introduction of a methyl group (2.1 G). Thus the different h.f.s. constants of the *meta*-protons observed in the *o*-methylbenzoyl radical [ $a(\text{H})$  1.7 and 0.4 G] demonstrate a different population of the isomers.

The e.s.r. spectrum of the radical (5) shows an additional proton splitting (Table) with respect to that of the *Z*-conformer of radical (1). It was assigned to the proton at position 5, since the *Z*-arrangement in (5) is more planar than in (1). Accordingly, INDO calculations, performed on the unsubstituted naphthoyl radical (1), predict that the h.f.s. constant at position 5 increases when the carbonyl group is in a planar situation rather than in a twisted conformation (Table: footnote).

The 4-methoxy-1-naphthoyl radical (9) exhibited, down to 213 K, a symmetric spectrum consisting of a quartet with  $a(3\text{H})$  0.7 G. In light of the empirical W-rule, the h.f.s. constants were attributed to the *Z*-conformer. Most likely the conformation of the acyl radical, in this case, depends upon that of the precursor aldehyde ( $\Delta G^\ddagger$  8 kcal mol<sup>-1</sup>), which was found to be essentially *Z*.<sup>13-15</sup> Since the conjugation between the carbonyl group and the naphthalene ring is increased with respect to that of the radical (1), owing to the resonance contribution by the methoxy substituent, the *Z*-arrangement is expected to be close to planar as in the radical (5). Our conclusions are supported by the detectable h.f.s. constant at position 5 (0.7 G). However, INDO calculations suggest that a more planar conformation involves also larger h.f.s. constants of the protons at positions 2 and 8; but, experimentally, the opposite behaviour leads us to

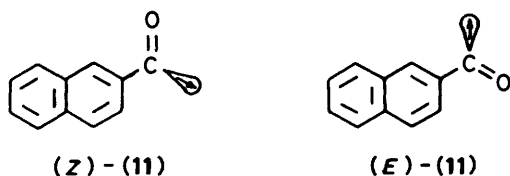
conclude that both the distortion of the carbonyl fragment and the electronic substituent effect contribute to modify the e.s.r. parameters.

The 4-methyl-1-naphthoyl radical (10) behaved in the same way as the unsubstituted derivative, showing a spectrum consisting of a triplet and a doublet of doublets at low temperature (143 K) with relative intensities 55:45.

**2-Naphthoyl Radicals.**—Photolysis of di-*t*-butyl peroxide in the presence of 2-naphthaldehyde in cyclopropane gave rise to a spectrum of one radical consisting of a doublet of doublets  $a(\text{H})$  0.4 and 2.0 G, over the range 137–218 K, as shown in Figure 2. Studies by n.m.r. spectroscopy have shown that in 2-naphthaldehyde the *E*-conformer is predominant (80% from dynamic n.m.r. measurements;<sup>13,15</sup> 86% from the lanthanide-induced shift method)<sup>14</sup> and the free energy of activation for *E*-to-*Z* exchange is 8.2 kcal mol<sup>-1</sup>.<sup>13</sup>

The real situation in the 2-naphthoyl radical (11) is likely to be rapid rotation about the C–CO bond. In fact, we have recently found<sup>10</sup> that the energy barrier in benzoyl  $\sigma$ -radicals is about 5 kcal mol<sup>-1</sup> lower than that in the corresponding aldehydes. If we reasonably assume that the same energy difference exists between the radical (11) and its parent molecule, the rotational barrier of the radical itself should be too low to be determined by e.s.r. techniques.

Thus the structure of the 2-naphthoyl radical (11) may be *Z* or *E*, or an equilibrium may exist between the two. In both structures the radical is assumed planar, as in the case of the benzoyl radical.



Theoretical and experimental attempts have been made to provide some indication of the conformational preference of this radical. First, the problem was approached by performing INDO calculations on the two possible planar conformations (Table). The experimental splittings seem to be more in agreement with INDO h.f.s. constants of the *Z*-rotamer (only a moderately large coupling at position 3) rather than with those of the *E*-rotamer (two quite large couplings at positions 1 and 4).<sup>\*</sup> These results indicate that the arrangement of the radical (11) is different from that of the parent aldehyde. On the other hand the  $\Delta G^\ddagger$  value of the molecule<sup>13</sup> (8.2 kcal mol<sup>-1</sup>) suggests that the conformational ratio of the radical may be mainly determined by that of the parent molecule. Thus, the theoretical approach cannot really contribute towards a true understanding of the problem. Analysis of the spectra of 1-methyl- and 3-methyl-2-naphthoyl radicals showed that the INDO approach is liable to give, in this case, misleading information. In fact, the 3-methyl-2-naphthoyl radical (12) displayed below 150 K a symmetric spectrum with  $a(3\text{H})$  0.5,  $a(\text{H})$  0.25, and  $a(\text{H})$  1.0 G.<sup>†</sup>

If the *Z*-arrangement in the radical (11) were the true situation, as suggested by INDO calculations, it would be more

favoured in the radical (12) owing to the presence of the alkyl group at position 3. However, in this case, only two small splittings should be observed: that of the methyl at position 3 and that of the proton at position 1 [ $a(\text{H})$  1.0 G could not be reasonably assigned].

In contrast, the trend of the h.f.s. constants of the radical (12) is clearly justified if an *E* arrangement (80%) in the radical (11) is assumed. As mentioned before, a methyl group modifies the conformational ratio of ca. 30–40%. Therefore the coupling,  $a(\text{H})$  1.0 G, can be thought of as the isotropic average of the splittings of the proton at position 4 which is involved in the two rapidly equilibrating planar forms, *Z* and *E*, in similar amounts (50;50). Further support for our observations comes from the analysis of the spectrum of the 1-methyl-2-naphthoyl radical (13): a doublet of doublets with  $a(\text{H})$  2.35 and 0.4 G. Owing to the steric effect of the alkyl moiety the *E*-conformation is the preferred one. As expected, the coupling at position 4 is almost equal to that found for the *E*-rotamer of the radical (11).

### Experimental

Some of the aldehydes were commercially available and were purified by distillation or chromatography before use. All the monomethyl-substituted naphthaldehydes were prepared from the corresponding dimethyl derivatives (commercially available) by the method described by Zalukaev and Moiseev,<sup>20</sup> as follows.

To a CCl<sub>4</sub> solution of the dimethylnaphthalene derivative (0.01M), *N*-bromosuccinimide (0.01M) was added. To the crude bromo derivative, hexamethylenetetramine (0.012M) in CHCl<sub>3</sub> (25 ml) was added, and the mixture was refluxed for 2 h; a white crystalline compound was filtered off. It was treated with AcOH (20 ml; 50%) for 1 h, and the monomethylnaphthaldehyde was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and NaHCO<sub>3</sub> (8%) to neutrality. Evaporation left a solid which was purified on a silica gel column eluted with CHCl<sub>3</sub>.

2,3-Dimethyl-1-naphthaldehyde was prepared following the method of Aslam *et al.*<sup>21</sup>

2-Deuterioxy-1-naphthaldehyde was obtained by dissolving the hydroxy compound in MeOD–CHCl<sub>3</sub> (1.5:2); the solution was left overnight, then the solvents were removed.

**E.s.r. Experiments.**—Samples of di-*t*-butyl peroxide and the aldehyde in cyclopropane were sealed under vacuum in Suprasil silica tubes and irradiated in the cavity of a Varian E-104 instrument with a 500 W mercury lamp. The *g* values for all the radicals examined are subject to an experimental error of ca.  $\pm 0.0002$ .

**INDO Calculations.**—INDO calculations were performed assuming  $d(\text{C}-\text{CHO})$  1.5 Å;  $d(\text{CO})$  1.22 Å, C–C=O angle 124°, and a normal geometry for the rest of the molecule:  $d(\text{CC}) = 1.4$  Å,  $d(\text{CH})$  1.08 Å, CCC and CCH angles 120°.

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\* A predominant planar form reproduces the experimental values better than the situation with two planar forms equally populated at equilibrium.

† The barrier to rotation about the C–CO bond in the radical (12) is expected to be lower than that in the unsubstituted one (11), so that only the region of fast exchange between *Z*- and *E*-rotamers is still being observed.

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