Acyl Radicals: the Relationship between Electron Spin Resonance Spectra, Structure, and Stability in a Family of σ-Radicals†

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A series of saturated and unsaturated acyl radicals, $R\dot{C}=O$, have been generated in fluid solution, principally by the photolysis of di-t-butyl peroxide in the presence of the corresponding aldehyde. Most of the acyl radicals show well-resolved hyperfine splittings, and the values of $a(H_\beta)$ correlate with the n.m.r. coupling constants $^3J(CHCHO)$ in the parent aldehyde. It is concluded that the acyl radicals and the corresponding aldehydes have similar structures.

EXTENSIVE studies have been carried out on the relationship between e.s.r. spectra, structure, and stability in carbon-centred π-radicals, and the steric and electronic factors which are involved are now fairly thoroughly understood.[1]

In contrast, there have been very few comparable studies of σ-radicals, largely no doubt because for two of the most important families, the vinyl radicals and the aryl radicals, the e.s.r. spectra are difficult to observe except under special conditions.

We describe here a study of this relationship for the acyl radicals, $R\dot{C}=O$. At the time when this work was started, the e.s.r. spectra of only 12 acyl radicals had been observed in solution.[2] The alkyl derivatives $R\dot{C}O$, R = Me, Et, Pr^i, Bu^t, and $PhCH_2$, had been prepared usually by photolysis of isopropyl, t-butyl, or benzyl ketones [equation (1)];[3] the fluoroalkyl derivatives, R = CF_3 and C_2F_5, by the reaction of t-butoxyl radicals with the appropriate aldehydes [equation (2)];[4] and the aryl derivatives, R = C_6H_5, *o*-FC_6H_4, *m*-FC_6H_4, *p*-FC_6H_4, and C_6H_5, by the same method [equation (2)].[5] No unsaturated acyl radicals had been reported.

$$RCOR' \xrightarrow{h\nu} R\dot{C}O + R''^{\bullet} \qquad (1)$$

$$Bu^tO\cdot + RCHO \longrightarrow Bu^tOH + R\dot{C}O \qquad (2)$$

Apart from the acetyl radical which showed a quartet spectrum,[3] the alkanoyl radicals were reported to show only broad (*ca.* 5 G) unresolved singlets, and this probably discouraged further studies. We find that these small alkanoyl radicals are exceptional and all the larger saturated ($R \geqslant C_5$) and all the 2,3-unsaturated acyl radicals show resolvable hyperfine coupling to the hydrogen on the β-carbon atoms.

We have prepared the acyl radicals usually by the reaction of t-butoxyl radicals with aldehydes [equation (2)], but in the case of the tri-t-butylbenzoyl radical, where the corresponding aldehyde is unknown, we have used instead the reaction between tributyltin radicals and the acyl chloride [equation (3); *cf.* ref. 6].

$$Bu_3Sn\cdot + RCOCl \longrightarrow Bu_3SnCl + R\dot{C}O \qquad (3)$$

EXPERIMENTAL AND RESULTS

Most of the aldehydes were commercially available, and were purified by distillation or by preparative g.l.c. before use. We are grateful to Dr. D. V. Banthorpe for the gift of samples of citral and citronellal.

t-Butylacetaldehyde.—3,3-Dimethylbutanol was oxidised with chromium trioxide and pyridine in dichloromethane by a general method,[7] giving the aldehyde in 30% yield, b.p. 146 °C, τ ($CHCl_3$) 0.25 (1 H, t, *J* 3.0 Hz, CHO), 7.95 (2 H, d, *J* 3.0 Hz, CH_2), and 9.15 (9 H, s, Bu^t).

Di-t-butylacetaldehyde.—This was prepared by Newman's method,[8] τ (CCl_4) 0.28 (1 H, d, *J* 6.0 Hz, CHO), 8.28 (1 H, d, *J* 6.0 Hz, C*H*CHO), and 8.92 (18 H, s, Bu^t).

Hex-5-enal.—This was prepared by the sequence of reactions: furfuryl alcohol ⟶ furfuryl chloride ⟶ pent-4-en-1-ol ⟶ 1-chloropent-4-ene ⟶ hex-5-enoic acid ⟶ hex-5-enoyl chloride[9] ⟶ hex-5-enal.[10] The aldehyde was purified by preparative g.l.c.

1-*Formylcyclopentene*.—The aldehyde was prepared by treating cyclohexane-1,2-diol with periodic acid.[11]

Hexanedial.—Oxidative ring-opening of cyclohexane-1,2-diol with lead tetra-acetate gave the dialdehyde,[12] b.p. 78 °C at 5 mmHg, τ (CCl_4) 0.21 (2 H, s, CHO), 7.3—7.9 (4 H, CH_2CHO), and 8.1—8.6 (4 H, CH_2CH_2CHO).

2,4,6-*Tri-t-butylbenzoyl Chloride*.—Tri-t-butylbenzene was prepared by the Friedel–Craft alkylation of benzene with t-butyl chloride in the presence of aluminium chloride, and converted into tri-t-butylbenzoyl chloride by Neckers' method.[13]

2-*Methylpent*-2-*enal*, 2-*Ethylhex*-2-*enal, and* 2-*Isopropyl*-5-*methylhex*-2-*enal*.—These 2-alkylalk-2-enals were prepared by the aldol condensation of the appropriate aldehydes.[14]

E.s.r. Experiments.—Samples of di-t-butyl peroxide and the aldehyde, or of hexabutylditin and the acyl halide, usually in cyclopropane solvent, were sealed in Suprasil silica tubes, and photolysed in the cavity of a Varian E4 e.s.r. spectrometer, with u.v. light from a 500 W a.c. Philips S.P. 500 or 500 W d.c. Philips CS 500 W/2 high pressure mercury arc. It is essential that high quality silica tubes should be used, because impurities give rise to an e.s.r. signal with a *g* value close to that of an acyl radical. The results are given in Tables 1 and 2.

INDO Calculations.—INDO Calculations were performed using a program modified from the standard CNINDO (obtainable from QCPE). We are grateful to Dr. A. R. Gregory for allowing us to use this program. The results are listed in Table 3.

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† Preliminary communication, A. G. Davies and R. Sutcliffe, *J.C.S. Chem. Comm.*, 1979, 473.

TABLE 1

N.m.r. coupling constants of aldehydes RCHO and e.s.r. spectra of the corresponding acyl radicals $R\dot{C}O$

		RCHO	$R\dot{C}O$				
Compound	R	^3J(CHCHO)	$a(H_\beta)$/G	ΔH_{pp}/G	$a(^{13}C)$/G	g	T/°C
(1)	CH_3	2.85	4.0 [a]	2.5		2.0005	−103
(2)	CH_3CH_2	1.31	<1.2 [a]	2.3		2.0006	−83
(3)	$CH_3CH_2CH_2$	1.69	*b*	1.9		2.0006	−75
(4)	$CH_3[CH_2]_2CH_2$	1.75	*c*	2.7	100.5	2.0007	−134
(5)	$CH_3[CH_2]_3CH_2$	1.73	*c*	1.5	120.2	2.0007	−129
			2.2 [e]	1.2		2.0007	−75
(6)	$CH_3[CH_2]_4CH_2$	1.7	2.18 [e]	0.7		2.0005	−52
(7)	$(CH_3)_2CHCH_2$	1.92	*b*	3.6		2.0005	−92
			2.15	1.0		2.0006	−75
(8)	$(CH_3)_3CCH_2$	2.92	3.8 [b]	1.2		2.0005	−94
(9)	$(CH_3)_2CH$	1.17	<1.5 [a]	2.3	113.6	2.0007	−95
			c	2.2		2.0006	−127
(10)	$[(CH_3)_3C]_2CH$	6.0	11.2 [d]	1.0	114.8	2.0005	−116
(11)	$(CH_3)_3C$		*a*	3.2		2.0008	−95
			c	3.0		2.0008	−130
(12)	$CH_2{=}CH(CH_2)_2CH_2$ [f]	*f*	*c*	2.05		2.0006	−89
(13)	$(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2$	2.05	3.06 (1 H)	1.4		2.0004	−126
			2.40 (2 H)	1.1		2.0004	−60
(14)	$OCH(CH_2)_3CH_2$	1.45	*g*	1.25	120.0	2.0006	−98

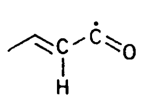
[a] By reaction (1) in methyltetrahydrofuran.[3] [b] By reaction (2) in iso-octane. [c] By reaction (2) in cyclopropane. [d] $da/dT = -18$ mG K^{-1}; *cf.* ref. 27. [e] By reaction (1) in cyclopropane. [f] Not resolved. [g] In toluene.

DISCUSSION

Although the quantitative agreement between the two methods is poor, both *ab initio* [15] and INDO (Table 3) calculations show that the linear structure of the acetyl radical (25), where $\angle C(2){-}\dot{C}(1){=}O = 180°$, should be less stable than the bent structures (22)—(24) in which $\angle C(2){-}\dot{C}(1){=}O = 124°$ as it does in acetaldehyde. This bent (*i.e.* σ) structure is confirmed by the high measured value of $a(^{13}C_\alpha)$ of *ca.* 125 G,[16] which is in keeping with calculations by both methods, and with qualitative

TABLE 2

N.m.r. coupling constants of 2,3-unsaturated aldehydes, and e.s.r. spectra of the corresponding acyl radicals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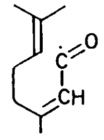
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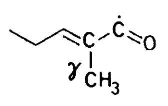
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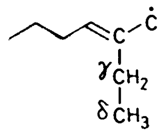
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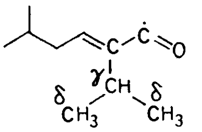
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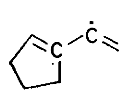
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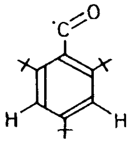
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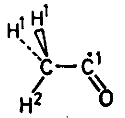
	RHCO	$R\dot{C}O$			
Acyl radical	^3J(CHCO)/ Hz	$a(H_\beta)$/G	ΔH_{pp}/ G	g	T/°C
(15)	7.74 ($1H_\beta$)	19.5 ($1H_\beta$)	0.9	2.0005	−119
(16)	8 ($1H_\beta$)	19.8 ($1H_\beta$)	1.2	2.0005	−126
(17)	1 ($3H_\gamma$)	1.10 ($3H_\gamma$)	0.4	2.0005	−119
(18)	1 ($1H_\gamma$)	2.22 ($2H_\gamma$)	0.9	2.0003	−122
		2.1 ($2H_\gamma$) 0.5 ($3H_\delta$)	0.3	2,0003	−68
(19)		7.4 ($1H_\gamma$) 0.4 ($6H_\delta$)	0.2	2.0005	−81
(20)			1.8	2.0003	−95
(21)		1.2 (2 H, m)	0.5	2.0005	−71

TABLE 3

INDO Calculations of e.s.r. hyperfine coupling constants on acyl radicals [a]



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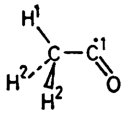

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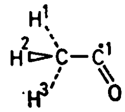

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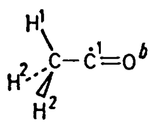

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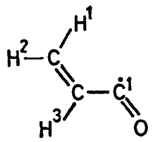

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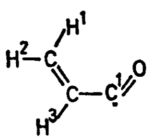

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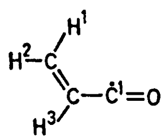

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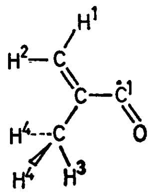

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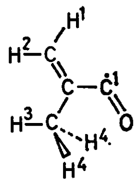

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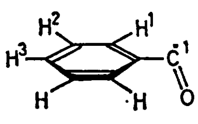


(31)

Radical	$a(H^1)$	$a(H^2)$	$a(H^3)$	$a(H^4)$	$a(^{13}C^1)$/ G
(22)	−1.26	23.25			127.31
(23)	3.80	8.27			127.51
(24)	1.68	0.16	18.68		127.40
(25)	46.47	12.48	12.48		28.59
(26)	0.00	0.51	26.66		130.10
(27)	1.05	9.58	−0.08		131.49
(28)	−9.99	−10.58	4.76		25.06
(29)	0.65	0.18	−0.08	1.93	133.15
(30)	0.64	0.19	4.23	−0.19	132.66
(31)	0.35	1.38	−0.83		110.35

[a] Assuming that $\angle C(2){-}C(1){=}O = 124°$, and that the other bond lengths and angles are the same as in the parent aldehydes. [b] Assuming that $\angle C(2){-}C(1){=}O = 180°$.

theory. It appears therefore that when reaction (2) occurs, the σ-CH bond containing an electron pair is replaced by the σ-orbital containing one unpaired electron, with little change in geometry at C(1).

Intramolecular interactions between the group R and the CH=O group in the aldehyde or the $\dot{\mathrm{C}}$=O group in the radical might therefore be expected to be similar, because they will be dominated by interactions involving the C=O group; those involving the σ-CH bond on the one hand or the singly occupied σ-orbital on the other being similar and relatively small. If this is so, any conformational characteristic of the group R with respect to the CHO group in the aldehyde should be retained in the acyl radical.

Spin–spin coupling between hydrogen nuclei in the group R and the unpaired electron of the acyl radical (Table 3 and ref. 15), or the proton of the aldehyde group,[17,18] is strongly dependent on the conformational relationship between R and the carbonyl group, and both $a(\mathrm{H}_\beta)$ and $^{3}J(\mathrm{C}H\mathrm{C}H\mathrm{O})$ show a similar dependence on the dihedral angle θ as defined in (I) and (II).

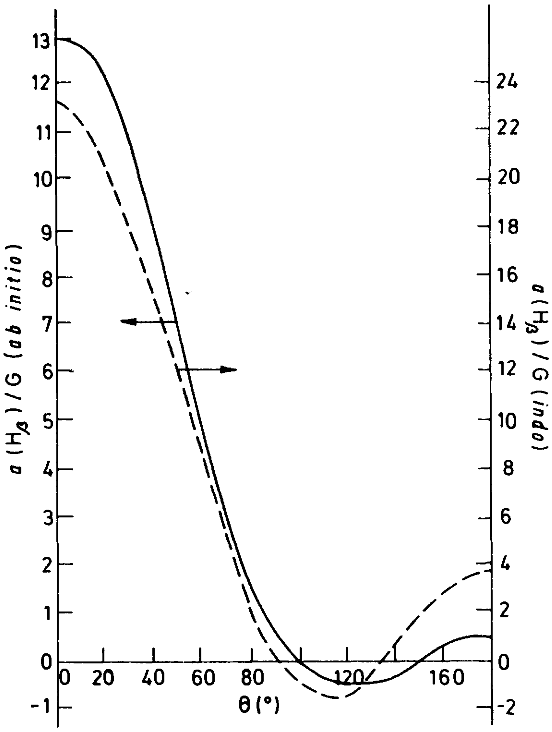


FIGURE 1 *Ab initio* (——) and INDO (— — —) calculated values of $a(\mathrm{H}_\beta)$ in the $\mathrm{CH_3\dot{C}O}$ radical as a function of the dihedral angle θ. The *ab initio* values are taken from ref. 15, and predict an average value of $a(3\mathrm{H}_\beta)$ of 4.9 G, against an experimental value of 4.0 G.[3] The INDO values are taken from Table 3, and predict that $a(3\mathrm{H}_\beta)$ should be 6.8 G

Figure 1 illustrates a plot against θ of the values of $a(\mathrm{H}_\beta)$ in the acetyl radical (I) calculated by *ab initio* [15] and INDO (Table 3) methods, taking ∠C(2)–C(1)=O = 124°, and Figure 2 shows the same function for values of $^{3}J(\mathrm{C}H\mathrm{C}H\mathrm{O})$ for a particular pair of protons in acetaldehyde (II), calculated by the INDO method.[17]

Both functions show a similar type of angular dependence, the coupling constants being at a maximum when the hydrogen atom in R is *trans* to the σ-bond or singly occupied σ-orbital (θ 0°), falling to a low minimum value when θ *ca.* 120°, and then rising to a low maximum when the hydrogen atom in R is in the *cis*-position (θ 180°).

If the conformations of the aldehyde and the derived acyl radical are indeed similar, one might therefore expect a rough correlation between the respective values of $^{3}J(\mathrm{C}H\mathrm{C}H\mathrm{O})$ and $a(\mathrm{H}_\beta)$.* This is borne out by Figure 3 where values of $^{3}J(\mathrm{C}H\mathrm{C}H\mathrm{O})$ and $a(\mathrm{H}_\beta)$ are plotted for various pairs of aldehyde and acyl radical, and the relationship $a(\mathrm{H}_\beta)/\mathrm{G} = 2.20\ ^{3}J(\mathrm{C}H\mathrm{C}H\mathrm{O})/\mathrm{Hz} - 1.98$ holds where R is a saturated alkyl group or a small homocyclic or heterocyclic ring; from the two examples which are available, it appears that the points for unsaturated aldehydes lie rather above this line.†

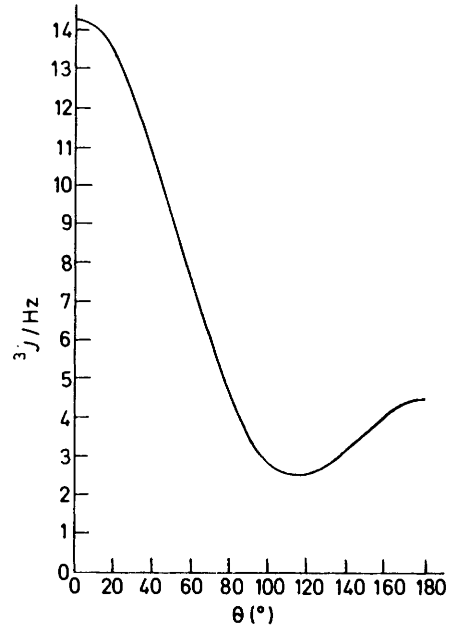
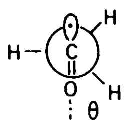
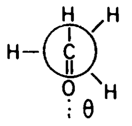


FIGURE 2 INDO Calculated values of $^{3}J(\mathrm{C}H\mathrm{C}H\mathrm{O})$ in acetaldehyde.[17] The calculations overestimate the average value of ^{3}J as 6.41 Hz, against the experimental value of 2.85 Hz. From measurements on a series of aldehydes, Karabatsos and Hsi [18] concluded that ^{3}J (θ 0°) = 7.6 Hz and ^{3}J (θ 180°) = 0.5 Hz, and that these values are reduced by 0.4 Hz for each alkyl substituent which is introduced at C(2)



(I)



(II)

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* The theoretical basis for the relationship between n.m.r. and e.s.r. coupling has been discussed by Dixon.[19] Previous examples include $^{3}J(HCCH)$ *versus* $a(\mathrm{H}_\beta)$ (in π-radicals),[20] $^{1}J(^{13}\mathrm{CH})$ *versus* $a(\mathrm{H}_\beta)$, $^{1}J(^{13}\mathrm{CH})$ *versus* $a(^{13}\mathrm{C}_\alpha)$, $^{2}J(\mathrm{HCH})$ *versus* $a(\mathrm{H}_\alpha)$,[21] and $^{1}J(^{31}\mathrm{P–H})$ *versus* $a(^{31}\mathrm{P})$.[22]

† Part of the reason for the deviation of points from the line is that the n.m.r. spectra have been measured near room temperature whereas many of the e.s.r. spectra can be recorded only at much lower temperature, and $a(\mathrm{H}_\beta)$ and $^{3}J(\mathrm{CHCHO})$ for the conformationally biased species may be strongly temperature-dependent.

In the discussion which follows, the results in Tables 1 and 2 are analysed on the basis of this model.

In acetaldehyde the rotational barrier about the C(1)–C(2) bond is 4.7 kJ mol^{-1}.[23] The three hydrogen atoms of the methyl group appear equivalent on the n.m.r. time scale at normal temperature and show a temperature-independent, averaged value for ^3J(CHCHO) of 2.9 G, which is high for a simple aldehyde. The corresponding acetyl radical (I) has a computed rotational barrier of 1.6 kJ mol^{-1},[15] and shows a spectrum which is clearly resolved into a quartet, $a(3H_\beta)$ 4.0 G, ΔH_{pp} *ca.* 2.0 G.[3]

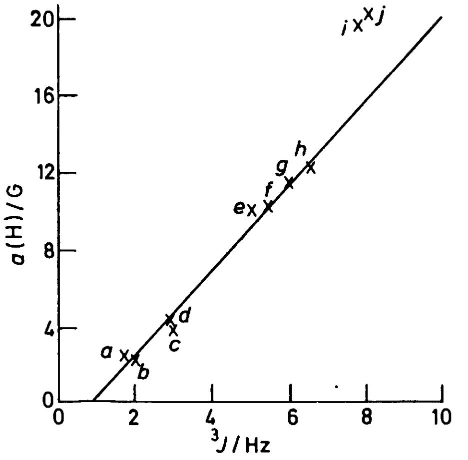


FIGURE 3 Plot of ^3J(C*H*CH*O*) in aldehydes against $a(H_\beta)$ in the corresponding acyl radicals. The values of ^3J are taken from G. K. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, 1965, **87**, 2854, or G. K. Karabatsos and D. J. Fenoglio, *J. Amer. Chem. Soc.*, 1969, **91**, 3577, or are our own measurements: *a*, Bu^tCH_2-CHO; *b*, Me_2CHCH_2CHO; *c*, Bu^tCH_2CHO; *d*, CH_3CHO; *e*, Bu^tNCH_2CHCHO; *f*, CH_2CH_2CHCHO; *g*, Bu^t_2CHCHO; *h*, OCH_2CHCHO; *i*, MeCH=CHCHO; *j*, $Me_2C{=}CH(CH_2)_2CMe{=}$CHCO

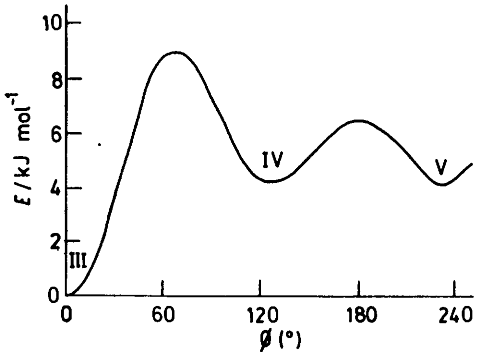
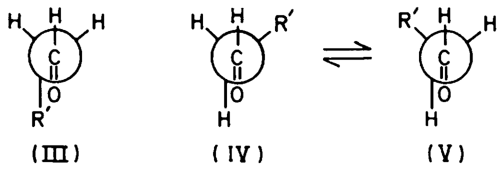


FIGURE 4 Potential energy of propionaldehyde as a function of the dihedral angle θ; taken from ref. 24

If a small alkyl group R′ of up to about three carbon atoms is introduced at C(2), the aldehyde is most stable in conformation (III) in which the carbonyl group eclipses the C–R′ bond;[18,24] rotation about the C(1)–C(2) bond generates the potential energy profile shown in Figure 4, which has two other lesser minima corresponding to the *gauche*-conformations (IV) and (V) at 120 and 240° respectively to the *cis*-form.[25]

The value of ^3J(CHCHO) in these aldehydes is consequently lower than in acetaldehyde (<1.8 Hz) as the preferred angle θ is 120°, and the coupling shows a positive temperature coefficient (*ca.* 3 × 10^{-3} Hz K^{-1}) as rotation becomes more free at high temperature.



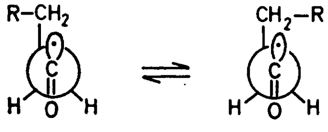
(4)

In accord with the above model, the corresponding acyl radicals [Table 1, (2)—(4), (9), (12), (14)] show broad singlets, ΔH_{pp} *ca.* 4 G, any hyperfine coupling being within the line width.

If the alkyl group is larger (R′ ⩾ C_4H_9), the value of ^3J(CHCHO) increases,[18] presumably because θ (av.) increases as steric repulsion between R′ and the carbonyl group begins to outweigh the effect which leads to eclipsing when R′ is smaller; the *gauche*-conformations (IV) and (V) are now preferred over (III). The corresponding acyl radicals (5)—(8), (10), and (13) now show observable hyperfine coupling with $a(2H_\beta)$ >2 G, and selective line broadening is apparent in some of the spectra at low temperature. The central line of the triplet in the heptanoyl radical (6) is broadened below −100 °C, and the radical (13) derived from citronellal shows at −60 °C the expected triplet from coupling by two β-hydrogen atoms, but at −126 °C, only a doublet is apparent.

Two types of restricted rotation could account for this line-broadening effect.

First, if the most stable conformation is now the *gauche*-structure (IV)—(V), restricted rotation about the C(1)–C(2) bond [(IV) ⇌ (V); equation (4)] may render the two hydrogen atoms non-equivalent at low temperatures, with broadening of the central line (M_I = O) of the triplet.



(5)

Secondly, if rotation about the C(1)–C(2) bond remains free, or if the most stable conformation is that in which the β-methylene protons are symmetrically placed with respect to the singly occupied σ-orbital (VI) and (VII), their coupling constants could yet undergo out-of-phase modulation if rotation about the C(2)–C(3) bond were restricted [equation (5)].* This would be equivalent to

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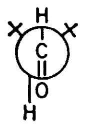
* Restriction of rotation about both the C(1)–C(2) and C(2)–C(3) bonds in the radical $CF_3CF_2\dot{C}O$ has been postulated, to account for the fact that one fluorine atom of the $\dot{C}F_3$ group shows a unique high coupling constant.[4]

the effect which leads to selective line-broadening in n-alkyl π-radicals.[1,26]

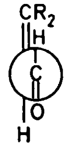
When $R' = Bu^t$ (8), ^3J(CHCHO) in the aldehyde is larger (*ca.* 2.9 Hz), implying that the time-averaged conformation is further biased away from the structure (III); the acyl radical shows a correspondingly high value for $a(2H_\beta)$ of 3.8 G at -94 °C, and now no alternating line width effect could be detected. Such an effect should still in principle be possible on the model of equation (4) but not on that of equation (5), but the Bu^t group may simply be too small to show the effect at an accessible temperature. More extensive studies will be needed before a choice can be made between these two models.

With two bulky substituents at C(2), the conformation (VIII) is preferred in which the C=O group is eclipsed by the β-C–H bond (θ 0°). In di-t-butylacetaldehyde, ^3J(CHCHO) is large (*ca.* 6.0 Hz at 35 °C) and shows a negative temperature coefficient, $dJ/dT = -4.5 \times 10^{-3}$ Hz K^{-1} over the range -30 to $+70$ °C.[18] Likewise the di-t-butylacetyl radical (10) shows a large value $a(H_\beta)$ of 11.2 G at -116 °C, with a negative temperature coefficient of -1.8×10^{-4} G K^{-1}; the value for $a(^{13}C_\alpha)$ of 114.8 G, which could be measured in natural abundance confirms that, despite the large value of $a(H_\beta)$, this is still a σ-radical.*

In 2,3-unsaturated aldehydes (Table 2), the C=C–C=O skeleton is held planar by conjugation between the olefinic and carbonyl π-systems, and the *s-trans* conformation (IX) is more stable than the *s-cis* (in acrolein itself by 13 kJ mol^{-1}).[28] In the n.m.r. spectra, ^3J(CH-CHO) has the large value of *ca.* 7 Hz, as is appropriate for *trans*-located hydrogens.



(VIII)



(IX)

The e.s.r. spectra of the corresponding vinylacyl radicals (15) and (16) similarly show large hyperfine coupling constants, $a(H_\beta)$ *ca.* 20 G. INDO Calculations (Table 3) show that the structures which are linear at C(1) (28) or *s-cis* about C(1)–C(2) (27) would have values of $a(H_\beta) < 5$ G, whereas the *s-trans* structures (26) should have $a(H_\beta)$ *ca.* 26 G, near the values which are observed. We conclude that these vinylacyl radicals obey our rule that the parent aldehyde and the product acyl radical should have corresponding structures.

2-Alkylacroleins have the same *s-trans* structure as acrolein itself, and the n.m.r. spectra show resolvable long-range coupling between the alkyl and formyl protons, with ^4J *ca.* 1 Hz. The e.s.r. spectra of the radicals derived from 2-methylpent-2-enal (17), 2-ethylhex-2-enal (18), and 2-isopropyl-5-methylhex-2-enal (19) similarly show hyperfine coupling to the three, two, or one γ-hydrogen atoms respectively, in the alkyl group. The radical (19) shows a remarkably large γ-coupling of 7.7 G at -117 °C, and at -81 °C even the coupling to the δ-hydrogen atoms (0.4 G) can be detected. INDO Calculations on the structures (29) and (30) suggest that the large γ-coupling probably comes from the proton adopting a W-conformation with respect to the singly occupied σ-orbital.

Studies by Krusic and Rettig[5] on the benzoyl and deuteriobenzoyl radicals showed that the equilibrium structure was planar, with a small rotational barrier about the C(1)–C(2) bond, so that coupling from the two *meta* protons (1.16 G) was equivalent down to -120 °C, when some broadening of the central line of the triplet occurred. We thought that the presence of bulky *ortho*-substituents might impose a non-planar conformation on the radical with some effect on the e.s.r. spectrum, but INDO calculations on the perpendicular structure (31) showed that the coupling from the *meta*-protons should still predominate, and the acyl radical (21) showed a normal triplet coupling of 1.2 G.

In a preliminary note[6] we have described the e.s.r. spectrum of the cyclopropylacyl radicals. Again the radicals are most stable in the same conformations as the parent aldehydes (see Figure 1), and now the e.s.r. spectra of distinct conformational isomers can be observed at low temperature, and the kinetics of their interconversion can be determined. We have since found the same phenomenon with the analogous heterocyclic oxiranylacyl and aziridinylacyl radicals. This work is continuing and will be reported separately.

It would be an obvious extension of the present work to look for a correlation between the structures of imidoyl radicals, $R\dot{C}{=}NR'$, and the corresponding imines, RCH=NR′, and although the number of examples which we have obtained is relatively small, the same relationship does indeed appear to hold.

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* Malatesta *et al.* have obtained the same radical by the photolysis of hexabutylditin and hydrogen iodide in the presence of di-t-butylketen, and report the same temperature dependence of $a(H_\beta)$.[27]

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