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MAGNETIC NON-EQUIVALENCE OF METHYL GROUPS AND X-RAY STRUCTURE OF TRICARBONYLCHROMIUM PHENYLISOPROPYLMETHYL SULFONIUM TETRAFLUOROBORATE

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Summary

The difference in chemical shifts between the two geminal methyl protons of the isopropyl groups of three sulfonium tetrafluoborates free and complexed with $Cr(CO)_3$, has been measured in a variety of solvents. The structure of tricarbonylchromium phenylisopropylmethyl sulfonium tetrafluoborate has been determined by a three-dimensional X-ray analysis. A tentative interpretation of the diastereotopic NMR shifts is given on the basis of the preferred conformations.

Introduction

Diastereotopic protons have been observed for a number of sulfonium salts by Mislow since 1967 [1]. For example, the chemical shift differences, Δ's, between the two geminal methyl groups in $Me_2CH\overset{+}{S}CH_3PhBF_4^-$ and $(Me_2CH)_2\overset{+}{S}PhClO_4^-$ are 0.18 and 0.19 ppm, respectively, in DMSO-d_6. The phenomenon has been observed also for methyl groups attached to sulfur in compounds of structure $Me_2\overset{+}{S}CHMePhBr^-$, with a marked solvent dependence arising from differences in conformational populations [2].

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In connection with our work on sulfonium ylides complexed with tricarbonylchromium [3], we have prepared some complexed sulfonium salts which contain diastereotopic protons. Specifically, tricarbonylchromium phenylisopropylmethyl sulfonium fluoborate shows chemical shift non-equivalence between the methyl groups of the isopropyl substituent. It seemed of interest to measure the effect of $Cr(CO)_3$ on the diastereotopy of the methyl groups by comparing the results for the complexed salt with those for the corresponding free ligand. The structure of the complexed salts has been determined by X-ray analysis, and this provides an important hint about the conformations assumed by the salt in solution.

Results

^{1}H NMR data

The tricarbonylchromiumphenylisopropyl methyl sulfonium fluoborate was prepared by methylation of tricarbonylchromiumphenylisopropyl sulfide with trimethyloxonium fluoborate in methylene chloride. The free sulfide was complexed with $Cr(CO)_6$ in diglyme at 160°C. The physical and spectroscopic characteristics of complexed and free sulfonium salts are reported in the Experimental section.

The ^{1}H NMR spectra of the sulphonium fluoroborates, $X{-}\overset{+}{S}MeCH(Me)_2\text{-}BF_4^-$, X = C_6H_5, $Cr(CO)_3C_6H_5$ and $(CH_3)_2CH$, were recorded in various solvents at a constant temperature. One of the more common features of the spectra of the complexed salt is the upfield shift of the aromatic protons of the coordinated ring (1.5—2 ppm). The pattern of the aromatic protons is quite similar to that shown by the aryl rings bearing a strongly electron-withdrawing substituent [4]. (See Experimental). The complexation of the ring with the metal does

TABLE 1

H NMR CHEMICAL SHIFTS [a] OF THE GEMINAL METHYL PROTONS FOR SULFONIUM FLUOBORATES OF STRUCTURE $X{-}S^+(Me)CHMe_2BF_4^-$ IN VARIOUS SOLVENTS [b] AT 296°K

Solvent (ε)	X = C_6H_5	X = π-$Cr(CO)_3C_6H_5$	X = Me_2CH
$CDCl_3$(4.8)	205.5 Δ = 26.0 179.5	[c]	201.8 Δ = 1.2 200.6
CD_2Cl_2(9.1)	196.4 23.8 172.6	194.4 Δ = 9.7 204.1	196.3 2.6 198.9
$CD_3\overset{O}{\overset{\|}{C}}CD_3$(20.3)	142.8 21.9 120.9	140.0 6.6 146.6	143.4 2.6 146.0
CD_3CN(36.2)	160.6 21.0 139.6	157.3 6.9 150.4	160.6 3.0 157.6
$CD_3\overset{O}{\overset{\|}{S}}CD_3$(48.9)	172.5 19.3 153.2	174.1 5.9 168.2	173.2 3.7 176.9

[a] In Hz downfield from external Me_4Si at 90 MHz. [b] The concentration of the salts was in the range 5 + 10% except in chloroform in which the concentration was much lower because the salts are only sparingly soluble. [c] Almost insoluble.

TABLE 2

CRYSTAL DATA

Molecular formula	$C_{13}H_{15}O_3SCr^+BF_4^-$
Molecular weight	390.15
Crystal size (mm)	0.20 X 0.20 X 0.25
Space group	*C*2/*c*
Cell constant (25°C)	
a (Å)	13.208 ± 0.004
b (Å)	13.061 ± 0.004
c (Å)	20.957 ± 0.006
β (°)	104.32 ± 15′
Unit cell volume (Å^3)	3503 ± 0.2
Density (calcd.)(g cm^{-3})	1.430 (*Z* = 8)
Linear absorption coeff. (Mo-K_α)(cm^{-1})	8.15
No. of reflections measured	3071
No. of reflections with $I > 3(I)$	938
$R = \|\|Fo\| - \|Fc\|\|/\|Fo\|$	0.147

not significally change the chemical shift of the α-methyl protons or of the methine proton of the isopropyl group (<0.1 ppm). The chemical shifts of the geminal methyls for the three salts and their difference, Δ, are reported in Table 1 for several solvents. Data have been collected also at various temperatures for the three salts: at −60—25°C in CD_3COCD and CD_2Cl_2, and 25—60°C in DMSO-d_6. Over these ranges no significant changes (ca. 1 Hz) of the chemical shift were observed.

X-ray data

The structure of the tricarbonylchromium phenylisopropylmethyl sulfonium fluoroborate has been elucidated by a three-dimensional X-ray structural analysis. The intensity data were collected at 25°C on a Philips PW 1100 computer-

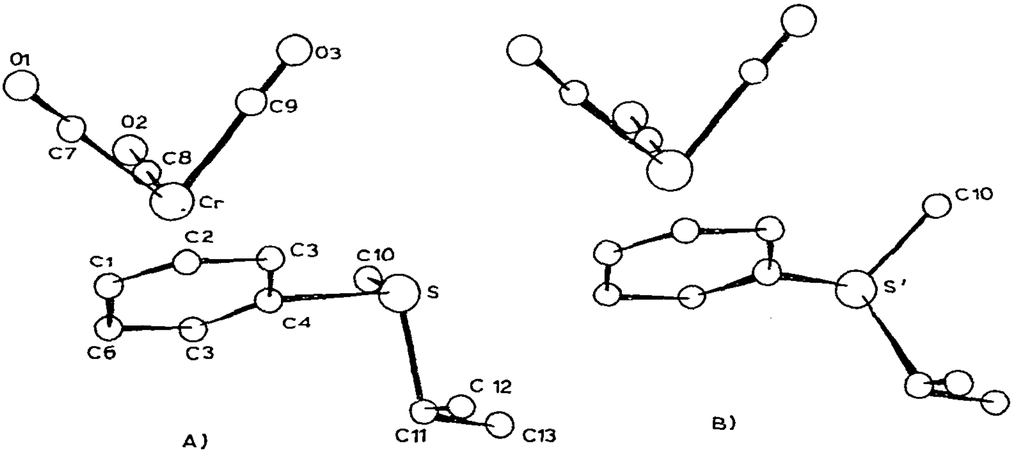

Fig. 1. Molecular structure of the two alternating units A and B. The methyl group in A is *trans-gauche* with respect to the isopropyl group; the methyl group in B (enantiomer of A) is *gauche-gauche* with respect to the isopropyl group.

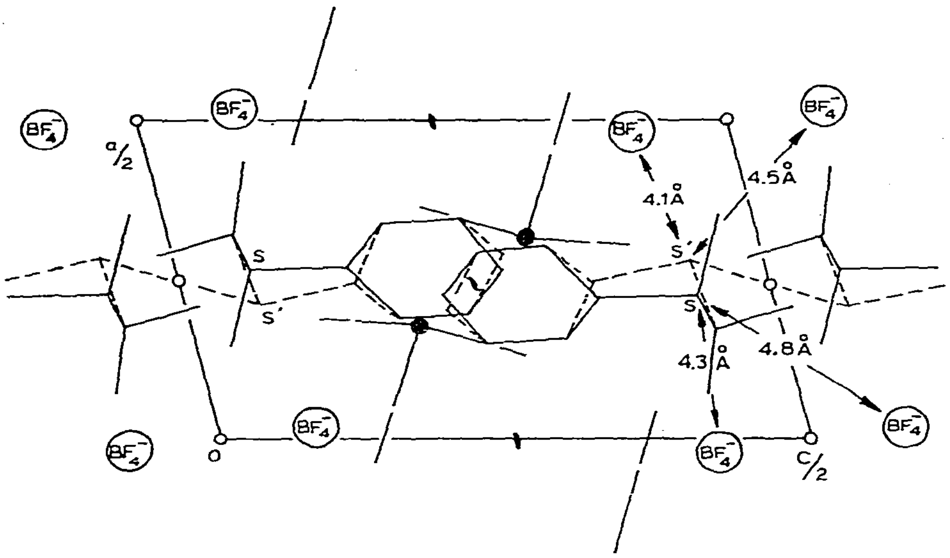

Fig. 2. Projection of the structure on (010): full line refers to model A, dashed line refers to model B.

controlled four-circle diffractometer with graphite monocromator; the θ—2θ scan method was used. The structure was refined by 8 cycles of full-matrix least square with isotropic thermal parameters to an R value of 0.18, 6 more cyles were calculated with anisotropic thermal parameters to the final R value of 0.147. The hydrogen atoms were not included in the calculations. Crystal data are reported in Table 2.

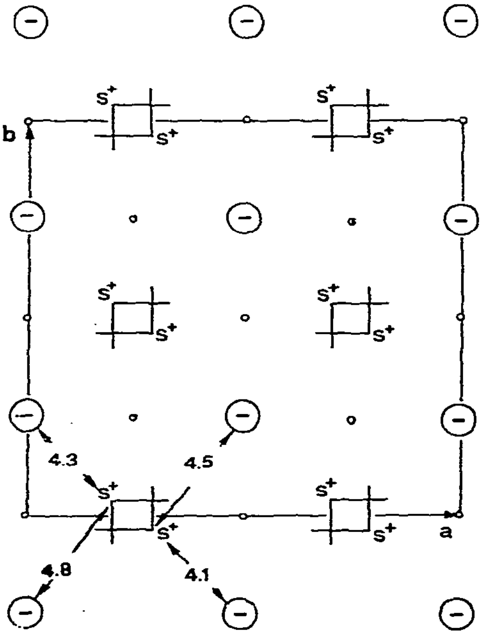

Fig. 3. The figure shows schematically the arrangement of opposite ions in the plane (001).

TABLE 3

FRACTIONAL ATOMIC COORDINATES (X10^4) AND THERMAL PARAMTERS (X10^3)[a,b,c]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	1804(4)	1709(4)	1936(3)	71(3)	78(4)	74(3)	−9(3)	18(2)	−27(4)
S	2079(14)	187(15)	620(8)	31(8)	100(15)	61(11)	−7(10)	0(9)	−28(11)
S′	7299(16)	606(16)	4402(10)	56(11)	76(15)	91(15)	3(11)	−1(11)	21(13)
O(1)	8686(24)	3191(24)	2121(15)	154(25)	122(26)	162(28)	114(22)	43(21)	81(22)
O(2)	456(21)	1446(28)	3725(16)	91(19)	222(38)	174(29)	53(23)	8(19)	71(27)
O(3)	8108(28)	3536(19)	3887(20)	197(32)	38(16)	293(46)	−4(19)	113(32)	11(23)
C(1)	7278(44)	905(49)	2212(19)	154(45)	227(62)	64(27)	−114(44)	64(33)	−62(36)
C(2)	6550(26)	1419(31)	2510(20)	76(24)	143(29)	58(24)	−63(26)	−20(20)	−12(26)
C(3)	6652(26)	1275(30)	3189(25)	72(24)	101(32)	119(39)	42(63)	−8(24)	3(28)
C(4)	7424(41)	602(39)	3531(18)	181(49)	137(45)	70(28)	−148(40)	55(33)	−26(31)
C(5)	8087(36)	97(30)	3236(17)	162(40)	98(30)	18(18)	−39(29)	−19(23)	−18(19)
C(6)	8023(35)	206(31)	2573(27)	112(35)	83(33)	140(50)	−9(27)	19(33)	4(31)
C(7)	8644(34)	2593(33)	2486(27)	121(35)	91(34)	206(53)	115(31)	−15(35)	38(35)
C(8)	9572(34)	1617(32)	3455(19)	130(35)	115(36)	131(35)	50(32)	28(29)	87(31)
C(9)	8162(27)	2805(28)	3621(19)	80(25)	52(22)	108(31)	7(23)	14(22)	30(24)
C(10)	8643(54)	343(49)	4742(32)	75(19)	—	—	—	—	—
C(10′)	7685(51)	1232(54)	4798(32)	80(21)	—	—	—	—	—
C(11)	6853(38)	−789(32)	4435(18)	197(46)	118(37)	89(30)	−29(34)	64(32)	64(27)
C(12)	5733(28)	−506(28)	4201(20)	74(25)	86(29)	166(40)	−5(22)	55(26)	−1(26)
C(13)	7110(40)	−1045(33)	5147(22)	251(55)	114(37)	141(41)	−89(37)	83(39)	18(31)
B	200(28)	2240(45)	5800(18)	229(42)	—	—	—	—	—
F(1)	1160(22)	2070(23)	6040(16)	169(27)	—	—	—	—	—
F(2)	90(37)	2230(44)	5230(17)	333(23)	—	—	—	—	—
F(3)	9760(29)	1710(31)	6170(20)	198(29)	—	—	—	—	—
F(4)	0000(29)	3260(30)	5950(19)	312(45)	—	—	—	—	—

[a] Estimated standard deviation in parentheses. [b] The thermal parameters U_{ij} (Å^2) are in the form $\exp[-2\pi^2(\Sigma_i\Sigma_j h_i h_j a_i^* a_j^* U_{ij})]$. [c] For C(10), C(10′), B, F(1), F(2), F(3) and F(4) the thermal parameters are isotropic.

The structure is characterized by a statistical alternation of two different molecular units, A and B (Fig. 1). In A the methyl group bonded to sulfur is in the conformation *trans-gauche* with respect to the isopropyl group; in the unit B, which is the enantiomer of A, the methyl group is in the non-equivalent conformation *gauche-gauche* with respect to the isopropyl group. These two almost isosterical units occupy statistically, in the ratio 1 : 1, the same position in the crystal. In both cases the coordination geometry of sulfur is pyramidal.

It is to be noted that the lone pair of S in B points toward the BF_4^- ions lined with *b* at (0*y*0) while in the case of A it points toward the BF_4^- ions lined with *b* at ($\frac{1}{2}$*y*0), as shown in Fig. 2. (The $\overset{+}{S}...BF_4^-$ interionic distances are listed in in the same figure.) As a result a homogeneous arrangement of the charges is achieved giving a nearly square planar network parallel to 001 of opposite ions, as shown schematically in Fig. 3. For the two alternate units, only S and its methyl group appeared resolved in the Fourier synthesis; the other corresponding atoms occupy positions very close to each other. We attribute their relative disorder to thermal anisotropy, which accounts for the high thermal parameters which are listed in Table 3 together with the final positional parameters. In addition this disorder associated with the sulphonium cations, the BF_4^- anions also show considerable disorder, as found in similar cases [e.g. 7]. The bond lengths B—F range between 1.17—1.41 Å and the thermal parameters of B and F are exceptionally high. These features account for the rapid drop of intensity with sin θ and the relatively high *R* value. Thus, no particular meaning can be

TABLE 4

SOME INTERNAL GEOMETRICAL PARAMETERS OF THE COMPLEXED SULFONIUM CATION (STANDARD DEVIATIONS ARE IN PARENTHESES)

Bond distances (Å)		Bond angles (°)	
Cr—C(7)	1.87(0.04)	C(7)—Cr—C(8)	90(4)
Cr—C(8)	1.80(0.04)	C(7)—Cr—C(9)	82(4)
Cr—C(9)	1.86(0.04)	C(8)—Cr—C(9)	89(4)
Cr—C(1)	2.17(0.05)	C(1)—C(2)—C(3)	118(4)
Cr—C(2)	2.23(0.05)	C(2)—C(3)—C(4)	119(4)
Cr—C(3)	2.19(0.06)	C(3)—C(4)—C(5)	123(4)
Cr—C(4)	2.14(0.05)	C(4)—C(5)—C(6)	122(4)
Cr—C(5)	2.15(0.05)	C(5)—C(6)—C(1)	118(4)
Cr—C(6)	2.20(0.06)	C(6)—C(1)—C(2)	121(4)
C(1)—C(2)	1.44(0.05)	C(4)—S—C(10)	94(3)
C(2)—C(3)	1.41(0.05)	C(4)—S—C(11)	98(2)
C(3)—C(4)	1.40(0.05)	C(10)—S—C(11)	95(3)
C(4)—C(5)	1.36(0.06)	C(4)—S'—C(10')	110(3)
C(5)—C(6)	1.38(0.05)	C(4)—S'—C(11)	103(3)
C(1)—C(6)	1.42(0.06)	C(4)—S'—C(11)	103(3)
C(7)—O(1)	1.11(0.05)	C(10')—S'—C(11)	109(3)
C(8)—O(2)	1.19(0.04)	C(12)—C(11)—C(13)	110(4)
S—C(4)	1.87(0.04)		
S—C(10)	1.77(0.07)		
S—C(11)	1.92(0.04)		
S'—C(4)	1.82(0.04)		
S'—C(10')	1.69(0.05)		
S—C(11)	1.92(0.05)		
C(11)—C(12)	1.49(0.05)		
C(11)—C(13)	1.49(0.05)		

attached to the geometrical parameters of the molecule found in this structural analysis (Table 4).

Discussion

The three magnetically non-equivalent conformations, excluding the eclipsed ones, are shown in Fig. 4, which makes use of Newman projections (I—III). The solid state structure is characterized, as we have seen, by the presence of two different conformations of each enantiomer, corresponding to conformations I and II. We suggest a tentative interpretation of the diastereotopic NMR shifts based on the working hypothesis that I and II are also the preferred conformations in solution for all three fluoborates studied in this work. The smooth and similar dependence of the diastereotopic shift on the nature of the solvent in all three cases supports the idea that no significantly different mechanisms are induced by solvent—solute interactions. Furthermore, since the steric requirements of isopropyl and phenyl groups are quite similar, it is reasonable that the two compounds should show similar conformational behavior. The presence of the complex $PhCr(CO)_3$ should not greatly alter the situation if the group (as is the case in the crystal) is *anti* with respect to the fixed isopropyl moiety.

Assuming equal populations of the two conformations, the diastereotopic shift for the geminal methyl groups is then given by

$$\Delta = \tfrac{1}{2}|(\delta_1 + \delta_3 - \delta_2' - \delta_1')|$$

and reduces to

$$\Delta = \tfrac{1}{2}|(\delta_3 - \delta_2')|$$

if one neglects the difference due to inversion at the prochiral carbon atom ($\delta_i = \delta_i'$).

The origin of the difference between δ_3 and δ_2' is in the first approximation the exchange of the X group with a methyl group between the *gauche* and the *trans* position relative to the methyl under consideration. We see that the largest effect occurs when X is a phenyl and the smallest when X is an isopropyl, the difference being one order of magnitude; the case for X = $PhCr(CO)_3$ is intermediate between the other two. In the presence of a phenyl group the difference may well be attributed to a ring current effect on δ_2' which is absent on δ_3. Measurement of the position of the pertinent hydrogen atoms on a constructed Dreiding model of conformation I (X = phenyl) produces an estimated * effect on δ_2' which is approximately the observed change of the diastereotopic shift on going from X = isopropyl to X = $PhCr(CO)_3$.

The difference in the chemical shift between the complexed and the uncomplexed phenyl derivatives is not explained, although a different rotational position of the phenyl ring around the carbon—sulfur bond might account for the effect.

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* The estimate is made by the use of Appendix B of reference 6. Averages are taken over the three methyl protons and the phenyl ring is considered fixed in a position such that the tricarbonylchromium is exactly *anti* to the isopropyl group.

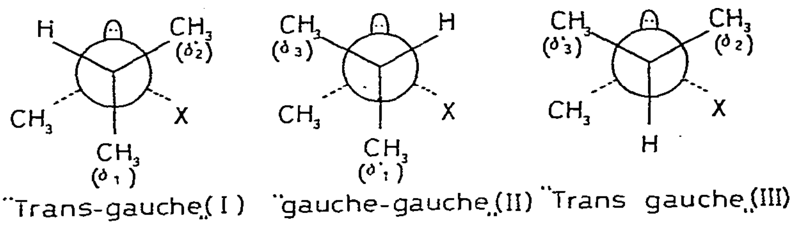

Fig. 4. Newman projections of sulfonium salts of structure X—$\overset{+}{S}$—(Me)CHMe$_2$ BF$_4^-$.

Complexation with Cr(CO)$_3$ does not influence the ring current as has been demonstrated in a seemingly conclusive manner through an "ad hoc" experiment by Keller [7].

In any case our discussion must be regarded as crude and qualitative in view of the oversimplification of the model which takes into account only ring current effects and neglects completely the presence of conformation III which is present to a certain extent in solution.

Experimental

Melting points are uncorrected. Microanalyses were performed by Mr. L. Turiaco, Instituto di Chimica Analitica, Padova, Italy.

The NMR spectra are recorded on a Bruker HFX-90 MHz spectrometer equipped with a Bruker B-St 100-700 temperature control unit.

Phenylisopropyl sulfide and diisopropyl sulfide were prepared by standard literature methods [8] and subsequently methylated to the corresponding sulfonium tetrafluoroborates by Me$_2$O$^+$BF$_4^-$ in anhydrous CH$_2$Cl$_2$ [9].

Phenylisopropylmethyl sulfonium tetrafluoborate. Oil. NMR (CD$_3$COCD$_3$): δ 7.78 (m, 5H, aromatic protons); 4.13 (sept, 1H, methine proton), 3.43 (s, 3H, $\overset{+}{S}$—CH$_3$ protons), 1.58 and 1.33 ppm (d, 3H each, diastereotopic CH$_3$ protons).

Diisopropylmethyl sulfonium tetrafluoroborate. White plates, highly higroscopic. No satisfactory elemental analysis was obtained. NMR (CD$_2$Cl$_2$): δ 3.71 (sept., 1H, methine proton), 2.70 (s, 3H, $\overset{+}{S}$-CH$_3$ protons); 1.51 and 1.48 ppm (d, 3H each diastereotopic CH protons).

Tricarbonylchromium phenylisopropyl sulfide

Phenylisopropyl sulfide-Cr(CO)$_3$ was prepared by refluxing under nitrogen for 12 h solutions of the free sulfide in anhydrous oxygen-free ethylene glycol dimethyl ether with an excess of freshly sublimed Cr(CO)$_6$. Column chromatography on neutral alumina (diethyl ether/hexane as eluent) gave the crude product which was crystallized from hexane under nitrogen to give yellow crystals. Yield, 9%; m.p. 49—50°C. Analysis, found: C, 50.20; H, 4.19, C$_{12}$H$_{12}$CrO$_3$S calcd.: C, 49.99; H, 4.20%. NMR (CD$_3$COCD$_3$): δ 5.36 (m, 6H, aromatic ring protons), 3.24 (sept, 1H, methine proton), 1.37 ppm (d, 5H, CH$_3$ protons).

Tricarbonylchromium phenylisopropylmethyl sulfonium tetrafluoroborate

Phenylisopropylmethyl sulfonium tetrafluoborate-Cr(CO)$_3$ was prepared from phenylisopropylsulfide-Cr(CO)$_3$ in anhydrous methylene chloride following Bunnett [9] and crystallized from absolute ethanol, giving yellow needles. Yield, 46%; m.p. 111–112°C. Analysis, found: C, 39.80; H, 3.79, $C_{13}H_{15}BCrF_4O_3S$ calcd.: C, 40.02; H, 3.87%. NMR (CD_3COCD_3): δ 6.49 (d, 2H, *ortho*-protons), 6.18 (t, 1H, *para*-proton), 5.77 (t, 2H, *meta*-protons), 4.26 (s, 3H, $\overset{+}{S}{-}CH_3$ protons), 3.43 (sept., 1H, methine proton), 1.66 and 1.58 ppm (d, 3H each, CH_3 protons).

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