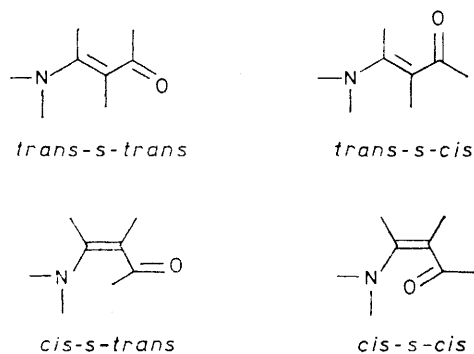


Nuclear Magnetic Resonance Spectral Study of β -Aminoenones

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The n.m.r. spectra of the four geometrical isomers of β -aminoenones, *trans-s-trans*, *trans-s-cis*, *cis-s-trans*, and *cis-s-cis*, are discussed. It was found that the chemical shift of the α -proton of β -aminoenones depends on both anisotropic effects and the electron density: $\delta = \delta_0 - \Delta\delta_{\text{struc}} = \Delta\delta_{\text{Ar}} + K(q - q_0)$. Thus the conformation of non-rigid β -aminoenones can be determined from the observed and the calculated chemical shifts of the α -proton.

WE are interested in the chemical behaviour of β -aminoenones which are known to have four geometrical isomers, *trans-s-trans*, *trans-s-cis*, *cis-s-trans*, and *cis-s-cis* (Scheme). These isomers have characteristic carbonyl



SCHEME

i.r. bands,¹ n.m.r. NH chemical shifts,^{1b,2} and u.v. absorption maxima.³

Pople proposed that chemical shifts depend on both anisotropic effects and electron density as expressed by formula (1).⁴ However, this formula is too complicated

$$\sigma_a = \sigma_{AA}^{\text{dia}} + \sigma_{AA}^{\text{par}} + \sum_{A=B} \sigma_{AB} + \sigma_A^{\text{deloc}} \quad (1)$$

to apply to complex systems such as β -aminoenones. We have used the simple formula (2) where δ is the chemical shift, σ_0 the chemical shift of a standard, $\Delta\delta_{\text{struc}}$ the anisotropic shift caused by geometrical factors from that of the standard, $\Delta\delta_{\text{Ar}}$ the anisotropic shift of aryl groups substituted into this system, K a constant, q the electron density on the adjacent carbon atom, and q_0 the electron density on the adjacent carbon atom of the standard.

$$\delta = \delta_0 - \Delta\delta_{\text{struc}} - \Delta\delta_{\text{Ar}} + K(q - q_0) \quad (2)$$

In this paper the applicability of formula (2) to the chemical shifts of the α -protons of β -aminoenones is discussed for 77 examples.

¹ (a) J. Darbrowski and K. K. Trela, *Spectrochimica Acta*, 1966, **22**, 211; (b) G. O. Dudek, *J. Org. Chem.*, 1965, **30**, 548.

² (a) G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, 1962, **84**, 2691; (b) H. W. Dürbeck and L. L. Duttka, *Tetrahedron*, 1973, **29**, 4285; (c) H. M. D. Brown and D. C. Nonhebel, *ibid.*, 1968, **24**, 5655; (d) D. L. Ostercamp, *J. Org. Chem.*, 1965, **30**, 1169.

³ (a) N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, 1949, **14**, 411; (b) C. Kashima, M. Yamamoto, and N. Sugiyama, *J. Chem. Soc. (C)*, 1970, 111.

⁴ J. A. Pople, *Proc. Roy. Soc.*, 1957, **A239**, 541.

⁵ A. E. Poland and W. R. Benson, *Chem. Rev.*, 1969, **69**, 161, and references therein.

EXPERIMENTAL

N.m.r. Measurements.—The n.m.r. spectra were recorded at 34° on a Hitachi R-20 60 MHz instrument with Me₄Si as internal standard and CDCl₃ as solvent. β -(Monosubstituted amino)- β -alkylenones which have a rigid *cis-s-cis* structure because of intramolecular hydrogen bonding between the carbonyl and amino-groups were used as the standard compounds.

Preparation of Samples.—Compounds (1)—(11) and (19) were prepared by the condensation of acetylacetone with the appropriate amines.^{2a,c,d} Similarly, compounds (12)—(18) and (24) were obtained from benzoylacetone and the appropriate amines.^{2c} Compounds (25)—(35) were synthesized by amine substitution of methyl⁵ and phenyl β -chlorovinyl ketones,⁵ respectively. Compounds (20)—(23) were prepared by hydrogenolysis of isoxazole derivatives.⁶ 2,3-Dihydropyridines (49)—(61) were prepared by the base-catalysed condensation of β -diketones with Schiff's bases.⁷ Compounds (62)—(63) were synthesized from acetylacetone and secondary amines,^{1a} and the preparation of (64)—(77) was carried out by the reaction of $\alpha\beta$ -unsaturated- β -chloro-ketones with secondary amines.⁵ Compounds (36)—(46) were, in each case, the sole product of the condensation of dimedone with the appropriate amine.^{2a,8} On the other hand, when *N*-methyl- and *N*-ethyl-aniline were treated with dimedone, two isomers (A and B) were obtained. These were identified as isomers of 5,5-dimethyl-3-(*N*-methylanilino)cyclohex-2-enone (47) and the *N*-ethyl-anilino-analogue (48) from the i.r. spectra and the elemental analysis.

Compound (47A and B).—Dimedone (1.4 g), *N*-methyl-aniline (1.2 g), and sulphuric acid (10 drops) in benzene (40 ml) were heated for 16 h under reflux with a Dean-Stark separator to remove water produced. The mixture was washed with water, dried (MgSO₄), and evaporated giving crude (47A and B). Recrystallization from benzene-*n*-hexane gave (47A) (1.8 g), m.p. 62° (Found: C, 78.55; H, 8.5; N, 6.0. C₁₅H₁₉NO requires C, 78.55; H, 8.35; N, 6.1%), ν_{max} (KBr) 1640 and 1610 cm⁻¹; and (47B) (0.2 g), m.p. 84° (Found: C, 78.55; H, 8.5; N, 6.0%), ν_{max} (KBr) 1640 and 1610 cm⁻¹.

Compound (48A and B).—Dimedone (2.8 g), *N*-methyl-aniline (2.4 g), and sulphuric acid (10 drops) in benzene (30 ml) were heated for 6 h under the same condition as above. Work-up gave (48A) (1.4 g), m.p. 108° (Found: C, 78.8; H, 8.65; N, 5.7. C₁₆H₂₁NO requires C, 78.95;

⁶ C. Kashima, S. Tobe, N. Sugiyama, and M. Yamamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 310; C. Kashima, N. Mukai, and Y. Tsuda, *Chem. Letters*, 1973, 539.

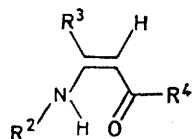
⁷ C. Kashima, M. Yamamoto, and N. Sugiyama, *Bull. Chem. Soc. Japan*, 1969, **42**, 1351; 1970, **43**, 901.

⁸ P. Crabbé, B. Halpern, and E. Santos, *Tetrahedron*, 1968, **24**, 4299; K. Yamada, T. Konakahara, and H. Iida, *Bull. Chem. Soc. Japan*, 1973, **46**, 2504.

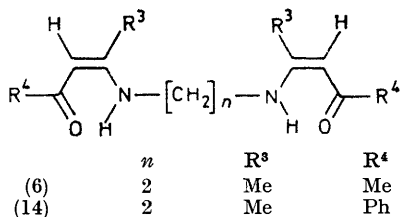
H, 8.7; N, 5.75%), ν_{\max} (KBr) 1650 and 1615 cm^{-1} ; and (48B) (0.54 g), m.p. 135° (Found: C, 78.8; H, 8.65; N, 5.7%), ν_{\max} (KBr) 1650 and 1615 cm^{-1} .

RESULTS

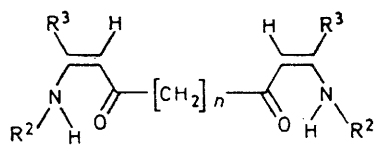
Determination of Structure of Compounds.—The n.m.r. spectra of compounds (1)–(35) show NH signals in the low field region, suggesting strong hydrogen bonding between the amino-group and the carbonyl oxygen atom. Therefore, these compounds are considered to have the *cis-s-cis*



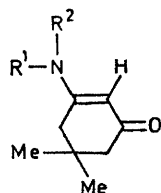
R ²	R ³	R ⁴	R ²	R ³	R ⁴	
(1)	Me	Me	(18)	<i>p</i> -NO ₂ C ₆ H ₄	Me	Ph
(2)	Pr	Me	(19)	H	Me	Me
(3)	Bu	Me	(24)	H	Me	Ph
(4)	PhCH ₂	Me	(25)	H	H	Me
(5)	Ph ₂ CH	Me	(26)	Me	H	Me
(7)	Ph	Me	(27)	Pr	H	Me
(8)	<i>p</i> -MeC ₆ H ₄	Me	(28)	Bu	H	Me
(9)	<i>p</i> -MeOC ₆ H ₄	Me	(29)	PhCH ₂	H	Me
(10)	<i>p</i> -ClC ₆ H ₄	Me	(30)	3,4-(MeO) ₂ C ₆ H ₃ -	H	Me
(11)	<i>p</i> -NO ₂ C ₆ H ₄	Me		[CH ₂] ₂		
(12)	Pr	Me	(31)	<i>p</i> -NO ₂ C ₆ H ₄	H	Me
(13)	PhCH ₂	Me	(32)	Me	H	Ph
(15)	Ph	Me	(33)	Et	H	Ph
(16)	<i>p</i> -MeC ₆ H ₄	Me	(34)	Pr	H	Ph
(17)	<i>p</i> -MeOC ₆ H ₄	Me	(35)	PhCH ₂	H	Ph



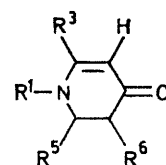
n	R ³	R ⁴
(6)	Me	Me
(14)	Me	Ph



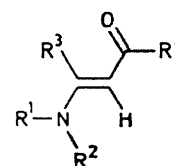
n	R ²	R ³
(20)	H	Me
(21)	H	Me
(22)	H	Me
(23)	H	Me



R ¹	R ²	R ¹	R ²
(36)	H	(44)	H
(37)	H	(45)	<i>m</i> -MeOC ₆ H ₄
(38)	H	(46)	[CH ₂] ₂
(39)	H	(47A)	Ph
(40)	H	(47B)	Ph
(41)	H	(48A)	Et
(42)	H	(48B)	Et
(43)	H		



	R ¹	R ³	R ⁵	R ⁶
(49)	H	Me	Ph	H
(50)	H	Me	PhCH ₂ CH ₂	H
(51)	H	Me	Ph	Me (<i>trans</i>)
(52)	H	Me	Ph	Me (<i>cis</i>)
(53)	H	Me	Me	PhCH ₂ CH ₂
(54)	Me	H	H	H
(55)	Ph	Me	Ph	H
(56)	Ph	Me	Ph	PhCH ₂ CH ₂
(57)	Ph	Me	Ph	PhCHOH
(58)	Ph	Me	PhCH=CH	H
(59)	Ph	Me	PhCH=CH	PhCH ₂ CH ₂
(60)	H	Ph	Ph	H
(61)	Ph	Ph	Ph	H



	R ¹	R ²	R ³	R ⁴
(62)	Et	Et	Me	Me
(63)		[CH ₂] ₄	Me	Me
(64)	Me	Me	Me	Ph
(65)	Et	Et	Me	Ph
(66)	Pr	Pr	Me	Ph
(67)	Me	Me	H	Me
(68)	Et	Et	H	Me
(69)	PhCH ₂	PhCH ₂	H	Me
(70)	Me	Me	H	Ph
(71)	Me	Et	H	Ph
(72)	Et	Et	H	Ph
(73)	Pr	Pr	H	Ph
(74)	Bu	Bu	H	Ph
(75)	Me	PhCH ₂	H	Ph
(76)	PhCH ₂	PhCH ₂	H	Ph
(77)		[CH ₂] ₄	H	Ph

structure.^{2c,3b} The structure of compounds (36)–(48) is fixed as *trans-s-trans* by the constraints of the ring system. Both the 4-H₂ and olefinic signals of (40)–(44), (47), and (48) (Table 1) are very similar. Compound (47B) is isomerized to (47A) upon heating in ethanol. These results suggest

TABLE 1

N.m.r. data for compounds (40)–(44), (47), and (48)

Compound	δ_{CH}	δ_{CH_2} (C-4)	δ_{CH_2} (C-6)	δ_{Me}
(40)	5.48	2.32	2.15	1.03
(41)	5.48	2.32	2.16	1.04
(42)	5.52	2.32	2.18	1.08
(43)	5.28	2.38	2.16	1.08
(44)	5.57	2.32	2.15	1.05
(47A)	5.51	2.32	2.23	1.07
(47B)	5.34	2.08	2.18	1.01
(48A)	5.50	2.49	2.20	1.00
(48B)	5.32	2.07	2.18	0.98

that (47A and B) are rotamers along the C–N single bond, which implies some twisting out-of-plane of the phenyl group (see later). By comparison of 4-H₂ and olefinic signals, compounds (40)–(44) were found to have the same rotational structure as (47A) and (48A). In both rotamers, the anisotropic effects of the benzene ring cannot be expected to affect the C-6 methylene protons. Thus, the signals of

TABLE 2
 Estimation of the anisotropic shift of the geometrical structural factor (δ_{struc}) C-CO-CH=C(-X³)-NX¹X²

Type	Isomer	X ¹	X ²	X ³	=O	=C	-C	-N:	Chelate	-X ³	-X ¹	-X ²	Total	(δ_{struc})
I	<i>c-s-c</i>	C	H	C	-0.10	-0.26	+0.02	-0.19	-0.14	+0.02	0	-0.01	-0.66	0
II	<i>c-s-c</i>	H	H	C	-0.10	-0.26	+0.02	-0.19	-0.14	+0.02	0	0	-0.65	+0.01
III	<i>c-s-c</i>	H	H	H	-0.10	-0.26	+0.02	-0.19	-0.14	0	0	0	-0.67	-0.01
IV	<i>c-s-c</i>	C	H	H	-0.10	-0.26	+0.02	-0.19	-0.14	0	0	-0.01	-0.68	-0.02
V	<i>c-s-c</i>	C	C	C	-0.10	-0.26	+0.02	-0.19	-0.14	+0.02	-0.02	-0.01	-0.68	0.02
VI	<i>c-s-c</i>	C	C	H	-0.10	-0.26	+0.02	-0.19	-0.14	0	-0.02	-0.01	-0.70	-0.04
VII	<i>t-s-t</i>	H	H	C	-0.19	-0.20	-0.02	-0.40	0	-0.02	+0.01	0	-0.82	-0.16
VIII-A	<i>t-s-t</i>	C	H	C	-0.19	-0.20	-0.02	-0.40	0	-0.02	+0.01	-0.02	-0.84	-0.18
VIII-B	<i>t-s-t</i>	C	H	C	-0.19	-0.20	-0.02	-0.40	0	-0.02	+0.08	0	-0.75	-0.09
IX	<i>t-s-t</i>	C	C	C	-0.19	-0.20	-0.02	-0.40	0	-0.02	+0.08	-0.02	-0.77	-0.11
X	<i>t-s-t</i>	C	C	H	-0.19	-0.20	-0.02	-0.40	0	0	+0.08	-0.02	-0.75	-0.09
XI	<i>c-s-t</i>	C	H	C	-0.19	-0.20	-0.02	-0.19	0	+0.02	-0.01	0	-0.59	+0.07
XII	<i>c-s-t</i>	C	C	C	-0.19	-0.20	-0.02	-0.19	0	+0.02	-0.01	-0.02	-0.61	+0.05
XIII	<i>c-s-t</i>	C	H	H	-0.19	-0.20	-0.02	-0.19	0	0	-0.01	0	-0.61	+0.05
XIV	<i>t-s-c</i>	C	C	C	-0.10	-0.26	+0.02	-0.40	0	-0.02	+0.08	-0.02	-0.70	-0.04
XV	<i>t-s-c</i>	C	C	H	-0.10	-0.26	+0.02	-0.40	0	0	+0.08	-0.02	-0.68	-0.02

δ 2.15—2.23 in the compounds (40)—(44), (47A and B), and (48A and B) were assigned to 6-H₂, on the basis of the established data for compound (36).⁹ On the other hand, the anisotropic effects of the benzene ring on 4-H₂ are expected to vary with the rotation along the C-N single bond. Since 4-H₂ signals of (47B) and (48B) appear to high field, the benzene ring of these compounds is assumed to be located near C-4. Moreover, by irradiation of the benzene ring protons of compound (40), the intensity of the 2-H signal increased by *ca.* 35%. A nuclear Overhauser effect for 4-H₂ was also observed upon irradiation of the benzene ring in compound (47B). These observations confirmed that the benzene ring of rotamer A is far from C-4 and that of B near C-4. Compounds (49)—(61) are of the *cis-s-trans* type. From the coupling constant of 3-H, the 2-aryl group is axial in all cases.⁷ The *N*-phenyl group of compounds (55)—(59) and (61) are considered to be equatorial in view of u.v. data⁷ and considerations of molecular models. A coupling constant between olefinic protons of 13 Hz suggests that compounds (67)—(77) have a *trans*-structure. Moreover, there is a sharp carbonyl absorption at *ca.* 1640 cm⁻¹ in compounds (67)—(77). Thus, these compounds are assumed to be *trans-s-cis*. Compounds (62)—(66) are also assumed to be *trans-s-cis* on the basis of the carbonyl band at *ca.* 1620 cm⁻¹. However, for compounds (62)—(77), there are not enough data to confirm the geometrical structure.

Anisotropic Effects.—The anisotropic effect was calculated by McConnell's equation¹⁰ (3) where θ and r were estimated

$$\sigma_{\Delta r} = \Delta\chi(1 - 3 \cos^2 \theta)/3r^3 \quad (3)$$

from molecular models and were applied to the data of Flygare¹¹ to give $\Delta\chi_{-H} - 0.3 \times 10^{-6}$, $\Delta\chi_{-C} - 1.1 \times 10^{-6}$, $\chi^2_{=O} - 2.9 \times 10^{-6}$, $\chi^2_{=C} - 3.5 \times 10^{-6}$, $\chi^2_{-C} - 7.4 \times 10^{-6}$, $\Delta\chi_{=O} - 6.2 \times 10^{-6}$, $\Delta\chi_{-N} - 12.5 \times 10^{-6}$, $\Delta\chi_{\text{chelate}} - 4.5 \times 10^{-6}$, and $\Delta\chi_{\text{Ar}} - 54 \times 10^{-6}$. The anisotropic shift for the geometric structural factor ($\Delta\delta_{\text{struc}}$) was estimated (Table 2) by counting the deviation from the standard *cis-s-cis* structure.

The anisotropic effects of the substituents excepting the aryl groups are negligible in all cases because of the long distance between the α -olefinic proton and the substituents. The estimated values of the anisotropic shifts of aryl groups ($\Delta\delta_{\text{Ar}}$) are listed in Table 3.

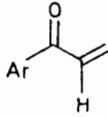
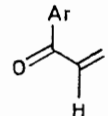
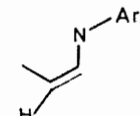
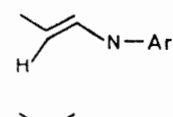
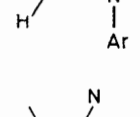
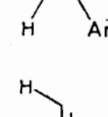
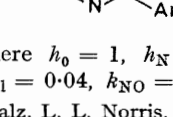
Electron Density of α -Protons.—The electron density of the β -aminoenones were calculated by the HMO method. The

⁹ J. V. Greenhill, *J. Chem. Soc. (C)*, 1971, 2699.

¹⁰ H. M. McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

treatment of a methyl group substituted into an aryl ring was carried out by using the hyperconjugation parameter while neglecting other groups in the system. The heteroatom parameters were as follows:¹² $\alpha = \alpha_0 + h_r\beta_0$;

 TABLE 3
 Estimation of the anisotropic shift of aryl group (δ_{Ar})

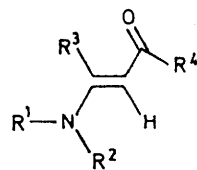
	- 0.58
	- 0.26
	- 0.17
	- 0.21
	- 1.37
	- 0.58
	- 0.10

$\beta_{\text{Cz}} = k_{\text{Cz}}\beta_0$ where $h_0 = 1$, $h_N = 1.5$, $h_{\text{Cl}} = 2$, $k_{\text{O=O}} = 1$, $k_{\text{O=N}} = 0.8$, $K_{\text{C=O}} = 0.04$, $k_{\text{N=O}} = 0.7$, and $k_{\text{O=Me}} = 0$. Thus,

¹¹ T. G. Schmalz, L. L. Norris, and W. H. Flygare, *J. Amer. Chem. Soc.*, 1973, **95**, 7961.

¹² A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 135.

TABLE 4
Electron density of α -carbon atom



R ¹	Substituents R ²	R ³	R ⁴	Electron density	-(q - q ₀)	-K(q - q ₀)
R*	R	R	R	1.1312	0	0
R	Ph	R	R	1.1250	0.0062	0.074
R	<i>p</i> -MeC ₆ H ₄	R	R	1.1264	0.0048	0.058
R	<i>p</i> -MeOC ₆ H ₄	R	R (45°) †	1.1285	0.0027	0.032
R	<i>p</i> -MeOC ₆ H ₄	R	R	1.1263	0.0049	0.059
R	<i>p</i> -MeOC ₆ H ₄	R	R (45°)	1.1284	0.0028	0.034
R	<i>m</i> -MeOC ₆ H ₄	R	R	1.1250	0.0062	0.074
R	<i>m</i> -MeOC ₆ H ₄	R	R (45°)	1.1277	0.0035	0.042
R	<i>p</i> -ClC ₆ H ₄	R	R	1.1254	0.0058	0.070
R	<i>m</i> -ClC ₆ H ₄	R	R	1.1250	0.0062	0.074
R	<i>m</i> -ClC ₆ H ₄	R	R (45°)	1.1277	0.0035	0.042
R	<i>p</i> -NO ₂ C ₆ H ₄	R	R	1.1120	0.0192	0.231
R	R	R	Ph	1.1273	0.0039	0.047
R	Ph	R	Ph	1.1205	0.0107	0.129
R	<i>p</i> -MeC ₆ H ₄	R	Ph	1.1128	0.0094	0.113
R	<i>p</i> -MeOC ₆ H ₄	R	Ph	1.1217	0.0095	0.114
R	<i>p</i> -NO ₂ C ₆ H ₄	R	Ph	1.1067	0.0245	0.294
R	R	Ph	R	1.1279	0.0033	0.040
R	Ph	Ph	R	1.1234	0.0078	0.094
R	Ph	R	R (30°)	1.1265	0.0047	0.056
R	Ph	R	R (45°)	1.1277	0.0035	0.042
R	Ph	R	R (60°)	1.1297	0.0015	0.018

* R = alkyl or H. † Angle between the aromatic ring and β -aminoenone system.

the electron density of the α -carbon atom of the standard structure (q_0) was estimated as 1.1312; those of the other systems are listed in Table 4.

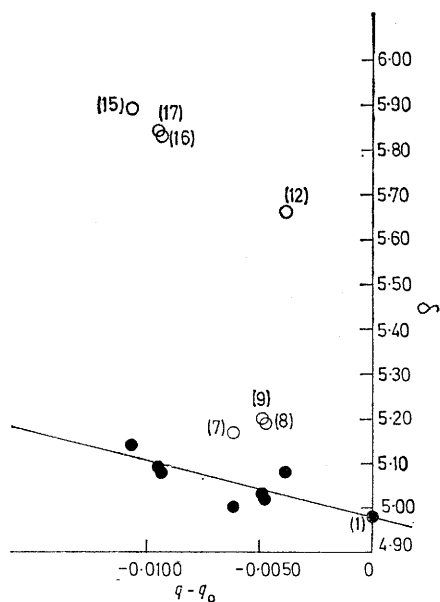
and $\Delta\delta_{\text{struc}}$ the anisotropic shift, while the values for aryl substituents ($\Delta\delta_{\text{Ar}}$) were taken from Tables 2 and 3. The

$$(\delta + \Delta\delta_{\text{struc}} + \Delta\delta_{\text{Ar}}) = K(q - q_0) + \delta_0 \quad (4)$$

electron density was taken from Table 4. The Figure gives a plot of $(\delta + \Delta\delta_{\text{struc}} + \Delta\delta_{\text{Ar}})$ against $(q - q_0)$. From the straight line, drawn by least squares, K was found to be -12.01 and δ_0 4.978.

DISCUSSION

The observed chemical shifts (δ_{obs}) of the α -olefinic proton of compounds (1)–(61), whose geometrical structures are fixed, are listed in Table 5. The calculated chemical shifts (δ_{calc}) of these compounds, derived by formula (2), are also listed in Table 5. In compounds (40)–(44), (47A), and (48A), intramolecular steric interaction between the *ortho*-proton of the benzene ring and olefinic proton at C-2 is expected from consideration of molecular models, if the benzene ring and aminoenone system are all in the same plane. The chemical shifts of 2-H of (40) and (47A) were calculated as δ 6.49 and 6.51 when the benzene ring and aminoenone system are in the same plane (observed δ 5.48 and 5.51, respectively). Thus, the benzene ring is assumed to be twisted. Therefore, the chemical shifts of the olefinic proton of compounds (40) and (47A) were calculated for the four different cases where the benzene ring is twisted by *ca.* 30, 45, 60, and 90° (see Table 5). Agreement between the calculated and observed chemical shifts was found for the benzene ring being twisted *ca.* 45° from β -aminoenone system.



Plot of $q - q_0$ against δ used for calculations of K and δ_0 :
○, δ_{obs} ; ●, $\delta + \Delta\delta_{\text{struc}} + \Delta\delta_{\text{Ar}}$

The Constant K .—In view of their fixed structures compounds (1), (7)–(9), (12), and (15)–(17) were chosen to derive the values of K and δ_0 . Formula (2) was modified to (4) where δ is the observed chemical shift of these compounds

TABLE 5

Observed and calculated chemical shifts of α -protons of compounds with fixed geometry

Compound	Type	δ_{struc}	δ_{Ar}	q	δ_{calc}	δ_{obs}	
(1)	I	0	0	1.1312	4.98	4.98	
(2)	I	0	0	1.1312	4.98	4.98	
(3)	I	0	0	1.1312	4.98	4.93	
(4)	I	0	0	1.1312	4.98	4.97	
(5)	I	0	0	1.1312	4.98	5.05	
(6)	I	0	0	1.1312	4.98	4.99	
(7)	I	0	-0.17	1.1250	5.22	5.17	
(8)	I	0	-0.17	1.1264	5.21	5.19	
(9)	I	0	-0.17	1.1263	5.21	5.20	
(10)	I	0	-0.17	1.1254	5.22	5.21	
(11)	I	0	-0.17	1.1120	5.38	5.40	
(12)	I	0	-0.58	1.1273	5.61	5.66	
(13)	I	0	-0.58	1.1273	5.61	5.73	
(14)	I	0	-0.58	1.1273	5.61	5.71	
(15)	I	0	-0.75	1.1205	5.86	5.89	
(16)	I	0	-0.75	1.1218	5.84	5.83	
(17)	I	0	-0.75	1.1217	5.84	5.84	
(18)	I	0	-0.75	1.1067	6.02	6.08	
(19)	II	+0.01	0	1.1312	4.97	5.01	
(20)	II	+0.01	0	1.1312	4.97	5.05	
(21)	II	+0.01	0	1.1312	4.97	5.02	
(22)	II	+0.01	0	1.1312	4.97	5.00	
(23)	II	+0.01	0	1.1312	4.97	5.00	
(24)	II	+0.01	-0.58	1.1273	5.60	5.70	
(25)	III	-0.01	0	1.1312	4.99	5.08	
(26)	IV	-0.02	0	1.1312	5.00	4.98	
(27)	IV	-0.02	0	1.1312	5.00	4.97	
(28)	IV	-0.02	0	1.1312	5.00	4.98	
(29)	IV	-0.02	0	1.1312	5.00	5.02	
(30)	IV	-0.02	0	1.1312	5.00	5.08	
(31)	IV	-0.02	-0.17	1.1120	5.40	5.47	
(32)	IV	-0.02	-0.58	1.1273	5.63	5.67	
(33)	IV	-0.02	-0.58	1.1273	5.63	5.69	
(34)	IV	-0.02	-0.58	1.1273	5.63	5.67	
(35)	IV	-0.02	-0.58	1.1273	5.63	5.74	
(36)	VIII-B	-0.09	0	1.1312	5.07	5.03	
(37)	VIII-B	-0.09	0	1.1312	5.07	5.08	
(38)	VIII-B	-0.09	0	1.1312	5.07	5.03	
(39)	VIII-B	-0.09	0	1.1312	5.07	4.95	
(40)	VIII-B	-0.09	-1.37	1.1250	6.49	5.48	
		-0.09	-0.94	1.1265	6.07	30° *	
		-0.09	-0.42	1.1277	5.53	45°	
		-0.09	+0.09	1.1297	5.00	60°	
		-0.09	+0.61	1.1312	4.46	90°	
(41)	VIII-B	-0.09	-0.42	1.1285	5.52	5.48	45°
(42)	VIII-B	-0.09	-0.42	1.1277	5.53	5.52	45°
(43)	VIII-B	-0.09	-0.42	1.1284	5.52	5.28	45°
(44)	VIII-B	-0.09	-0.42	1.1277	5.53	5.57	45°
(45)	IX	-0.11	0	1.1312	5.09	5.02	
(46)	VIII-B	-0.09	0	1.1312	5.07	5.17	
(47A)	IX	-0.11	-1.37	1.1250	6.51	5.51	0° *
		-0.11	-0.94	1.1265	6.09	30°	
		-0.11	-0.42	1.1277	5.55	45°	
		-0.11	+0.09	1.1297	5.02	60°	
		-0.11	+0.61	1.1312	4.48	90°	
(47B)	IX	-0.11	-0.21	1.1250	5.37	5.34	0°
(48A)	IX	-0.11	-0.42	1.1277	5.55	5.50	45°
(48B)	IX	-0.11	-0.21	1.1250	5.37	5.33	0°
(49)	XI	+0.07	-0.10	1.1312	5.01	4.93	
(50)	XI	+0.07	0	1.1312	4.91	4.90	
(51)	XI	+0.07	-0.10	1.1312	5.01	4.97	
(52)	XI	+0.07	-0.10	1.1312	5.01	4.95	
(53)	XI	+0.07	-0.10	1.1312	5.01	4.95	
(54)	XIII	+0.05	0	1.1312	4.93	4.85	
(55)	XII	+0.05	-0.27	1.1250	5.27	5.09	
(56)	XII	+0.05	-0.27	1.1250	5.27	5.23	
(57)	XII	+0.05	-0.27	1.1250	5.27	5.31	
(58)	XII	+0.05	-0.17	1.1250	5.17	5.18	
(59)	XII	+0.05	-0.17	1.1250	5.17	5.20	
(60)	XI	+0.07	-0.68	1.1279	5.63	5.46	
(61)	XII	+0.05	-0.85	1.1234	5.87	5.60	

* Angle between the benzene ring and β -aminoenone system.

The observed chemical shifts of compounds (1)—(61) are generally in fair agreement with the calculated values (± 0.06 p.p.m.). However, in the cases of compounds (5), (30), (35), (39), and (57)—(59), the differences are > 0.06 . All have either benzyl or phenethyl groups. However, the conformation of the benzene ring of these groups cannot be elucidated, while the anisotropic effect (δ_{Ar}) also cannot be estimated accurately. In these cases, the anisotropic effect of the benzene ring was omitted from the calculated chemical shifts.

Whether compounds (67)—(77) have the *trans-s-trans*- or *trans-s-cis*-structure could not be elucidated from i.r. and u.v. spectral data. Similarly, there are not enough data to elucidate the structure of compounds (62)—(66). The chemical shift of compounds (67)—(77) was calculated by formula (2) as arising from *trans-s-trans*- and

TABLE 6

Observed and calculated chemical shifts of α -protons of compounds with non-rigid geometry

Compound	Type	δ_{struc}	δ_{Ar}	q	δ_{calc}	δ_{obs}
(62)	V	-0.02	0	1.1312	5.00	5.09
	IX	-0.11	0	1.1312	5.09	
	XII	+0.05	0	1.1312	4.93	
	XIV	-0.04	0	1.1312	5.02	
(63)	V	-0.02	0	1.1312	5.00	4.95
	IX	-0.11	0	1.1312	5.09	
	XII	+0.05	0	1.1312	4.93	
	XIV	-0.04	0	1.1312	5.02	
(64)	V	-0.02	-0.26	1.1273	5.31	5.62
	IX	-0.11	-0.26	1.1273	5.40	
	XII	+0.05	-0.58	1.1273	5.56	
	XIV	-0.04	-0.58	1.1273	5.65	
(65)	V	-0.02	-0.26	1.1273	5.31	5.73
	IX	-0.11	-0.26	1.1273	5.40	
	XII	+0.05	-0.58	1.1273	5.56	
	XIV	-0.04	-0.58	1.1273	5.65	
(66)	V	-0.02	-0.26	1.1273	5.31	5.71
	IX	-0.11	-0.26	1.1273	5.40	
	XII	+0.05	-0.58	1.1273	5.56	
	XIV	-0.04	-0.58	1.1273	5.65	
(67)	X	-0.09	0	1.1312	5.07	5.07
	XV	-0.02	0	1.1312	5.00	
(68)	X	-0.09	0	1.1312	5.07	5.10
	XV	-0.02	0	1.1312	5.00	
(69)	X	-0.09	0	1.1312	5.07	5.31
	XV	-0.02	0	1.1312	5.00	
(70)	X	-0.09	-0.26	1.1273	5.38	5.68
	XV	-0.02	-0.58	1.1273	5.63	
(71)	X	-0.09	-0.26	1.1273	5.38	5.70
	XV	-0.02	-0.58	1.1273	5.63	
(72)	X	-0.09	-0.26	1.1273	5.38	5.75
	XV	-0.02	-0.58	1.1273	5.63	
(73)	X	-0.09	-0.26	1.1273	5.38	5.72
	XV	-0.02	-0.58	1.1273	5.63	
(74)	X	-0.09	-0.26	1.1273	5.38	5.72
	XV	-0.02	-0.58	1.1273	5.63	
(75)	X	-0.09	-0.26	1.1273	5.38	5.72
	XV	-0.02	-0.58	1.1273	5.63	
(76)	X	-0.09	-0.26	1.1273	5.38	6.02
	XV	-0.02	-0.58	1.1273	5.63	
(77)	X	-0.02	-0.26	1.1273	5.38	5.65
	XV	-0.09	-0.58	1.1273	5.63	

trans-s-cis-structures. In a similar manner, each of four chemical shifts was calculated for compounds (62)—(66). These results (Table 6) suggest that the preferred conformation of compounds (62)—(77) can be predicted. Compounds (62) and (67)—(69) are *trans-s-trans* and

(63)—(66) and (70)—(77) are *trans-s-cis*. These predictions are also supported by the i.r. carbonyl bands and the coupling constants of olefinic protons in the n.m.r. spectra and by molecular models.

In conclusion, the chemical shifts of β -aminoenones, whose geometry is fixed, can be calculated from formula (2). Moreover, in the cases of non-rigid β -aminoenones,

the conformation structure can be estimated from the differences in the observed and calculated chemical shifts of the α -proton.

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