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# Nuclear Magnetic Resonance and Infrared Spectra of some Aldimines (Azomethines)

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N.m.r. and i.r. spectra are reported for 19 imines of the type PCH=N-CHQR (P = alkyl or aryl and Q, R = (H,alk), (alk,alk), or  $-[CH_2]_n$ ). The variation in  $|J_{ab}|$  with structure is examined, and evidence is found for conformational effects similar to those for allylic coupling. The C=N stretching frequencies fall into characteristic and separate ranges for P = alkyl and P = aryl but finer effects are not generally apparent.

THE conformation-dependence of allylic <sup>1</sup>H<sup>-1</sup>H spinspin coupling is well established, both theoretically and experimentally.<sup>1-4</sup> The  $\pi$ -electron contribution to  $J_{ab}$ in structure (I) varies approximately as  $\cos^2 \phi$  and is considerably larger in magnitude than the σ-bond contribution. Thus,  $J_{ab}$  varies from slightly positive (ca. 0.5 Hz) for  $\phi = 90$  or 270° to substantially negative



(ca. -3 Hz) for  $\phi = 0$  or  $180^{\circ}$ . The distinction between cisoid and transoid coupling is not very great and is easily masked.<sup>2</sup> If restricted rotation occurs about the bond C(2)-C(3) then changes in the substituents  $R^2$  and  $R^3$ will cause differences in population of the various conformations and hence changes in the coupling between H<sup>a</sup> and H<sup>b</sup>. For example,  $|J_{ab}|$  is considerably smaller for CH2:CH•CHBut2 than for CH2:CH•CHMe2, because the t-butyl groups force H<sup>b</sup> predominantly into the eclipsed position with  $\phi \approx 90^{\circ.3}$ 

Such effects are expected to operate in other related systems such as the aldimines or azomethines (II). Although a number of n.m.r. spectra of such compounds have been published, there has been little discussion of this point. Hine and Yeh<sup>5</sup> studied the spectra of five aliphatic aldimines with a proton at H<sup>b</sup> and interpreted their results in terms of conformational effects similar to those discussed above, and Sternhell<sup>1</sup> has included imines in a general discussion of long-range coupling. We have carried out studies to establish these effects for the whole class of aldimines, and now report on the spectra of 19 imines carrying a wide variety of aliphatic, alicyclic, and aromatic substituents.

### EXPERIMENTAL

Imines were prepared by reactions of the appropriate aldehyde and amine.<sup>6</sup> Typically, the aldehyde was added slowly to an equimolar quantity of amine at 0° with shaking, reaction being complete after 2 hr. Products were dried

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 S. Sternhell, Rev. Pure Appl. Chem., 1964, 14, 15.
 G. P. Newsoroff and S. Sternhell, Tetrahedron Letters, 1968, 6117.

<sup>3</sup> A. A. Bothner-By, C. Naar-Colin, and H. Günther, J. Amer. Chem. Soc., 1962, 84, 2748.

 $(MgSO_4)$  and distilled under reduced pressure. Purity (as judged by n.m.r. and i.r. spectroscopy) was initially good for the benzaldehyde derivatives, although they deteriorated slowly on storage. The aliphatic imines were frequently less pure, being unstable to distillation even at low pressure, and deteriorating rapidly on storage even at  $ca. -10^{\circ}$ . The presence of solid potassium hydroxide during the drying and distillation was helpful.

N.m.r. spectra were recorded on a Perkin-Elmer R10 instrument operating at 60.00 MHz and/or a Varian HA 100 instrument at 100.00 MHz, usually at ambient temperature. Samples were neat liquids or 20-40% by volume solutions, usually in carbon tetrachloride, and tetramethylsilane was used for an internal reference. I.r. spectra in the range 625-4000 cm.<sup>-1</sup> were recorded for capillary films with a Perkin-Elmer model 257 spectrophotometer; band positions are accurate to 1-2 cm.<sup>-1</sup>.

#### RESULTS

The spectra obtained are described in abbreviated form below, and features of interest will be elaborated in the Discussion. The data given for each region of absorption are assignment, band position  $(\tau)$ , structure of band, and derived coupling constant moduli (Hz); assignments were usually supported by the correct integrated peak areas, which are not quoted.

 $C_{6}H_{5}-CH=N-CH_{2}-CH_{3}$  (60 and 100 MHz): a 1.92, t,  $J_{ab}$ 1.3; c 2.15—2.35 and 2.6—2.85, comp; b 6.52, qd,  $J_{bd}$  7.3,  $J_{ba}$  1.3; d 8.79, t,  $J_{db}$  7.2. On irradiation at  $\tau$  1.92 the H<sup>b</sup> band became a simple quartet  $(J_{bd} 7.3)$ ; on irradiation at  $\tau$  6.52 the Ha band became a singlet.

 $C_{6}H_{5}-CH=N-CH_{2}-CH_{2}-CH_{3}$  (60 and 100 MHz): *a* 1.93, t,  $J_{ab}$  1.4; c 2.15-2.35 and 2.5-2.9, comp; b 6.57, td,  $J_{bd}$ 6.8,  $J_{\rm ba}$  1.4;  $d \sim 8.32$ , asym tq,  $J_{\rm db} \approx J_{\rm de} \approx 7$ ;  $e \sim 9.09$ , asym t,  $J_{\rm ed} \approx 7$ . On irradiation at  $\tau 1.93$  the H<sup>b</sup> band became a simple triplet; on irradiation at  $\tau$  6.57 the H<sup>a</sup> band became a singlet.

 $C_6H_5$ -CH=N-CH<sub>2</sub>-CH(CH<sub>3</sub>)<sub>2</sub> (60 MHz): a 1.88, t,  $J_{ab}$  1.4; c 2·24—2·44 and 2·66—2·81, comp; b 6·66, dd,  $J_{bd}$  6·3,  $J_{ba}$ 1.4;  $d \, 8.06$ , d of sept,  $J_{\rm db} \approx J_{\rm de} \approx 6.3$ ;  $e \, 9.04$ , d,  $J_{\rm ed} \, 6.3$ .

 $C_{6}H_{5}^{c}-CH=N-CH_{2}^{o}-C_{6}H_{5}^{a}$  (60 MHz): *a* 1.98, t,  $J_{ab}$  1.4; *c* and d 2.15-2.38 and 2.65-2.95, comp; b 5.41, d,  $J_{ba} 1.4$ .

 $C_6H_5$ -CH=N-CH(CH<sub>3</sub>)<sub>2</sub> (60 MHz): *a* 1.88, s; *c* 

<sup>4</sup> M. Barfield, J. Chem. Phys., 1964, 41, 3825; 1968, 48, 4463; E. W. Garbisch, J. Amer. Chem. Soc., 1964, 86, 5561; E. B. Whipple, J. H. Goldstein, and G. R. McClure, *ibid.*, 1960, 82, 3811.

<sup>5</sup> J. Hine and C. Y. Yeh, *J. Amer. Chem. Soc.*, 1967, **89**, 2669. <sup>6</sup> R. W. Layer, *Chem. Rev.*, 1963, 489; M. M. Sprung, *ibid.*, 1940, **26**, 297; B. K. Campbell, K. N. Campbell, and A. H. Sommers, J. Amer. Chem. Soc., 1944, 66, 82.

 $C_{6}H_{5}$ -CH=N-CH(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub> (60 MHz): a 1.91, s; c 2.14—2.36 and 2.64—2.89, comp; b 7.22, quin,  $J_{bd}$  6.1; d 8.46, asym qd,  $J_{db} \approx 6.1$ ,  $J_{de} \approx 7.0$ ; *e* 9.18, asym t,  $J_{ed}$  7.0. No evidence of coupling between H<sup>a</sup> and H<sup>b</sup>.

b  $C_{6}H_{5}$ -CH=N-CH(CH<sub>2</sub>)<sub>5</sub>-(60 and 100 MHz): *a* 1.86, s; *c*  $2 \cdot 2 - 2 \cdot 5$  and  $2 \cdot 6 - 2 \cdot 9$ , comp; b  $6 \cdot 7 - 7 \cdot 1$ , broad and comp; d 8.0 - 8.9, broad and comp. On irradiation at  $\tau ca. 8.5$  the H<sup>b</sup> band became a singlet. The H<sup>a</sup> band was sharp, with no indication of coupling to H<sup>b</sup>.

 $C_{6}H_{5}-CH=N-CH(CH_{2})_{4}$  (60 MHz): *a* 1.88, s; *c* 2.2-2.5 and 2.6-2.85, comp;  $b \ 6.2-6.6$ , broad and comp;  $d \ 8.1-6.6$ 8.5, comp. No indication of coupling between H<sup>a</sup> and H<sup>b</sup>.

 $C_{6}H_{5}$ -CH=N-CH(CH<sub>2</sub>)<sub>2</sub> (60 MHz): *a* 1.85, s; *c* 2.35-2.52 and 2.75-2.95, comp; *b* 7.22, tt,  $J_{bd}$  6.4,  $J_{bd'}$  3.2; *d* and *d'* 9.0-9.3, comp. No indication of coupling between H<sup>a</sup> and H<sup>b</sup>.

 $p-Cl-C_{6}H_{4}-CH=N-CH_{2}-CH_{2}-CH_{3}$  (60 MHz): *a* 1.81, t,  $J_{ab}$  1·3; c 2·15-2·45 and 2·6-2·8, comp; b 6·49, td,  $J_{bd}$ 6.8,  $J_{\text{ba}} \stackrel{1.3}{_{c}}$ ;  $\frac{d}{a} \stackrel{8.31}{_{a}}$ , qt,  $J_{\text{de}} \stackrel{7.0}{_{b}}, J_{\text{bd}} \stackrel{6.8}{_{f}}$ ; e 9.07, t,  $J_{\text{ed}} 7.0$ .  $p - CH_3O - C_6H_4 - CH = N - CH_2 - CH_2 - CH_3 (60 \text{ MHz}): a 1.85, t,$  $J_{ab} \approx 1.3; d 2.12 - 2.41 and 3.0 - 3.3, comp; c 6.28, s;$ b 6.51, td,  $J_{be} \approx 6.7$ ,  $J_{ba} \approx 1.4$ ; e 8.32, sext,  $J_{db} \approx J_{de} \approx 7$ ; 9.09, asym t,  $J_{ed} \approx 7.0$ .

CH<sub>3</sub>-CH<sub>2</sub>-CH=N-CH<sub>2</sub>-CH<sub>3</sub> (60 and 100 MHz): a 2.39, tt,  $J_{\rm ad}$  4·1,  $J_{\rm ab}$  1·1; b 6·71, qd,  $J_{\rm be}$  7·3,  $J_{\rm ba}$  1·1; d 7·85, qd,  $J_{\rm dc}$ 7.3,  $J_{da}$  4.1; c and e 8.89 and 8.97, two t's,  $J_{od} \approx J_{eb} \approx 7.5$ .

 $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$  (60 MHz): a 2.41, t,  $J_{\rm ad}$  4.3; b 6.75, t,  $J_{
m be}$  6.7; d 7.47, qd,  $J_{
m dc} \gtrsim$  6,  $J_{
m da} \gtrsim$  4; e  $8\cdot 2$ — $8\cdot 8$ , asym qt; c and f  $8\cdot 8$ — $9\cdot 3$ , comp. H<sup>a</sup> and H<sup>b</sup> both show fine structure which could be due to  $J_{\rm ab} \simeq 1$  and/or coupling to the CH<sub>3</sub> groups; evidence not conclusive.

 $a_{c}^{a} = b_{d}^{a} = b_{d}^{c} = c_{d}^{a} = c_{d}^{c} = c_{d$ qt,  $J_{ac}$  4·5,  $J_{ab}$  1·1; b 6·79, t of comp,  $J_{bd}$  6·3,  $J_{ba} \approx J_{be} \approx 1$ ; c 8.15, d,  $J_{\rm ca}$  4.4; d 8.60, asym qt,  $J_{\rm db} \approx J_{\rm de} \approx 6.6$ ; e 9.16, asym td,  $J_{\rm ed}$  7.0,  $J_{\rm eb} \approx 1$ .

 $CH_{3}^{\mu}-CH_{2}^{\mu}-CH_{2}^{\mu}-CH_{3}^{\mu}-CH_{3}^{\mu})_{2}$  (60 MHz): *a* 2.47, t,  $J_{ae}$  4.7; b 7.2—7.8, comp; e 7.7—8.2, comp; d and f 8.2—8.8, comp; c and g 8.9—9-4, comp. No indication of coupling between H<sup>a</sup> and H<sup>b</sup>.

 $(CH_3)_2CH-CH=N-CH(CH_2-CH_3)_2$  (60 and 100 MHz): *a* 2.60, d,  $J_{ad}$  4.5; b 6.81, quin,  $J_{be}$  6.0; d 7.3—7.8, comp; e ~8.56, ~quin,  $J_{eb} \approx J_{ef} \approx 6$ ; c and f 8.9—9.4, comp. No indication of coupling between H<sup>a</sup> and H<sup>b</sup>.

 $CH_3-CH_2-CH=N-CH(CH_2)_5-$  (60 and 100 MHz): a 2.36, t,  $J_{\rm ad}$  4·3; b 6·8—7·4, comp; d 7·84, asym dq,  $J_{\rm da}$  4·2,  $J_{\rm dc}$ 7.2; e 8.0—9.0, comp; c 8.98, asym t,  $J_{cd}$  7.5. H<sup>a</sup> and H<sup>c</sup> showed further splitting consistent with  $J_{ac} \simeq 0.6$ . Probably no coupling between H<sup>a</sup> and H<sup>b</sup>, but not conclusive.

 $\overset{c}{\operatorname{CH}}_{3}^{d} \overset{a}{\operatorname{CH}}_{2}^{e} \overset{b}{\operatorname{CH}}_{2}^{e} \overset{c}{\operatorname{CH}}_{2}^{e} \overset{b}{\operatorname{CH}}_{2}^{e} \overset{c}{\operatorname{CH}}_{2}^{e} (100 \text{ MHz}): a 2.39, t, J_{ad} 4.3;$ b, 7.41, tt,  $J_{be}$  6.2,  $J_{be'}$  4.0; d 7.97, qd,  $J_{de}$  7.5,  $J_{da}$  4.3; c 9.12, t.  $J_{cd}$  7.5; e and e' 9.3-9.6, comp. On irradiation at  $\tau$  7.97 the Ha and Hc bands became sharp singlets; on irradiation at  $\tau$  7.41 the  $\mathrm{H}^{e,e'}$  bands collapsed.

 $(CH_3)_2CH-CH=N-CH(CH_2)_2 \rightarrow (60 \text{ and } 100 \text{ MHz}): a 2.40,$ d,  $J_{ad}$  4.5; b 6.82, comp; d 7.65, sept of d,  $J_{dc}$  6.7,  $J_{da}$  4.3; c 8.98, d,  $J_{cd}$  6.8; e and e' 9.18, comp. No indication of coupling between H<sup>a</sup> and H<sup>b</sup>.

### DISCUSSION

The discussion will be restricted in the main to those features common to all the compounds studied, namely the C=N stretching frequency and the n.m.r. parameters related to H<sup>a</sup> and H<sup>b</sup> in structure (III), *i.e.*  $\tau_a$ ,  $\tau_b$ , and

### TABLE 1

Comparative data for the compounds  $\ensuremath{\mathsf{PCH=N-CHQR}}$ 

Р	Q, R	$\tau_{\mathbf{a}}$	$\tau_{\rm b}$	$ J_{ab} /Hz$	ν̄ <sub>(C=N)</sub> /cm1
Ph	H. Me	1.92	6.52	1.3	1650
Ph	H, Et	1.93	6.57	1.4	1647
Ph	H, Pr <sup>i</sup>	1.88	6.66	1.4	1646
Ph	H, Ph	1.98	5.41	1.4	1650
Ph	Me, Me	1.88	6.60		1648
Ph	Et, Et	1.91	7.22		1647
Ph	-[CH.]	1.86	$\sim 6.9$		1648
Ph	-[CH,]	1.88	$\sim 6.4$		1648
Ph	-[CH,],-	1.85	7.22		1636
b-ClC <sub>a</sub> H <sub>a</sub>	H, Et	1.81	6.49	1.3	1647
b-MeÖ•C <sub>e</sub> H₄	H, Et	1.85	6.51	1.3 - 1.4	1646
Et	H, Me	2.39	6.71	1.1	1670
Et	H, Et	2.41	6.75	~1?	1667
Me	H, Et	2.43	6.79	1.1	1669
Pr <sup>n</sup>	Et, Et	2.47	$\sim 7.5$		;
Pr <sup>i</sup>	Et, Et	2.60	6.81		1671
Et	-[CH <sub>2</sub> ] <sub>5</sub> -	2.36	$\sim 7.1$	?	1670
Et	-[CH,],-	2.39	7.41	atu	1660
Pri	-[CH2]2-	$2 \cdot 40$	6.82		1662

? = Not recorded, or interpretation not certain. - = Noindication of coupling;  $|J_{ab}| < ca. 0.5$  Hz.

 $|J_{ab}|$ . These results are collected in Table 1. The other spectral features were much as expected and showed

## (III) P-CH<sup>a</sup>=N-CH<sup>b</sup>QR

no abnormalities. Relevant n.m.r. data from the literature are given in Table 2.

C=N Stretching Frequency.—The results obtained here fall, with only three exceptions, into the ranges previously reported 8 for compounds of the types Alk-CH:- $N \cdot Alk(1669 + 2 \text{ cm}^{-1} \text{ here, } cf. 1665-1674 \text{ cm}^{-1})$  and Ar•CH:N•Alk (1648  $\pm 2$  cm.<sup>-1</sup> here, cf. 1629–1656 cm.<sup>-1</sup>). The lower values for the aromatic compounds presumably reflect some delocalisation of the C=N electrons by conjugation with the ring. The exceptions mentioned above are the three N-cyclopropyl compounds, in which  $\bar{v}$ (C=N) is ca. 10 cm.<sup>-1</sup> lower than for the other corresponding compounds, possibly because of conjugation between the C=N bond and the cyclopropyl group.<sup>9</sup>

<sup>9</sup> See, for example, C. H. Heathcock and S. R. Poulter, J. Amer. Chem. Soc., 1968, 90, 3766, and references cited therein.

<sup>&</sup>lt;sup>7</sup> J. F. King and T. Durst, *Canad. J. Chem.*, 1962, **40**, 882. <sup>8</sup> J. Fabian, M. Legrand, and P. Poirier, *Bull. Soc. chim. France*, 1956, 1499; L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1958, and references cited therein.

Chemical Shift  $\tau_a$ .—The chemical shift of the proton in the PCH=N- group is characteristic of whether P is alkyl ( $\tau_a = 2.37 - 2.52$  in 15 out of 18 cases) or aryl  $(\tau_a = 1.81 - 1.93$  in 13 out of 15 cases). The greater variability of  $\tau_a$  for aromatic imines in general is attributable to conjugative effects on the electron distribution, as evidenced by correlations of  $\tau_a$  with the Hammett  $\sigma\text{-constants}$  of substituents in the aromatic systems of imines of the type Ar•CH:N•Ar.<sup>10,11</sup> The lower values of

though there is a tendency for it to increase when Q = His replaced by Q = Alk.

Coupling Constant  $J_{ab}$ .—The results reveal a strong correlation between  $|J_{ab}|$  ( $J_{ab}$  is presumed to be negative 1,4) and the nature of Q,R, as shown in Table 3. Thus the observations of Hine and Yeh<sup>5</sup> are now extended to cover the whole range of aldimine structures. By analogy with their discussion the present compounds are thought to exist entirely as the trans-

	R	elevant published da	ita *			
P Me Et Pr <sup>i</sup> Ph	Q H H H H	R H H H H	$\tau_{a}$ 2·30 2·40 2·50 1·81	ть 6·78 6·83 6·84 6·53	J <sub>ab</sub>  /Hz 1.8 2, 1.6 1.6 1.6	Ref. a 5 b
-CPh·CH <sub>2</sub> ·CH <sub>2</sub>	н н	н	2·3 2·43	6·8 6·83	1·3 1·5	c d
$-C[C_6H_3(OMe)_3]CH_2 \cdot CH_2$ Me $Pr^i$ $Pr^i$ $Pr^i$ Bu <sup>t</sup>	H H H H H H	H Me Et Pr <sup>n</sup> Pr <sup>n</sup>	3·73 2·37 2·51 2·52 2·51 2·51 2·52	$6 \cdot 14$ $6 \cdot 70$ $6 \cdot 72$ $6 \cdot 75$ $6 \cdot 70$ $6 \cdot 65$	1.3 1.5 1.3 1.4 1.3 $\sim 1.5$	e a 5 5 5 f
-CPh·CH <sub>2</sub> ·CH <sub>2</sub>	Н Н	Ph CH]	2·20	5·49 6·08	1·2 ?	d ø
$L^{OH_{3}} O^{O_{6}H_{3}}$ $Pr^{i}$ $Bu^{t}$ $o-HO \cdot C_{6}H_{4}$ $Ph$ Alk	Me Me Me CO <sub>2</sub> Me Ph	Me Et Me CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ·OH CHPh·N:CHAlk	2·49 2·50 2·22 2·11 1·5-2·6 '	6·80 7·10 7·04 5·72 ?	<0·5 ? ~0? ? ?	s f h i j

TABLE 2

\* Cyclic imines are not included.

<sup>6</sup> N. Colebourne, R. G. Foster, and E. Robson, J. Chem. Soc. (C), 1967, 685. <sup>b</sup> K. Tori, M. Ohtsuru, and T. Kubota, Bull. Chem. Soc. Japan, 1966, **39**, 1089. <sup>e</sup> M. Ahlbrecht, J. Blecher, and F. Kröhnke, Tetrahedron Letters, 1969, 439. <sup>d</sup> R. V. Stevens, M. C. Ellis, and M. P. Wentland, J. Amer. Chem. Soc., 1968, **90**, 5576. <sup>e</sup> R. V. Stevens and M. P. Wentland, J. Amer. Chem. Soc., 1968, **90**, 5576. <sup>e</sup> R. V. Stevens and M. P. Wentland, J. Amer. Chem. Soc., 1968, **90**, 5580. <sup>f</sup> R. Bonnett, J. Chem. Soc., 1965, 2313. <sup>e</sup> NMR Spectra Catalogue, Varian Associates, 1963, No. 673. <sup>h</sup> J. J. Charette, Spectrochim. Acta, 1963, **19**, 1275. <sup>f</sup> Ref. g No. 663. <sup>f</sup> H. A. Staab, F. Vögtle, and A. Mannschrak, Tetrahedron Letters, 1965, 697.

 $\tau_a$  for P = Ar compared with P = Alk are in line with the similar difference found in olefins.<sup>12</sup>

### TABLE 3

Correlation of  $J_{ab}$  with structure

Q,R <b>≠</b>	$ J_{ab} /Hz$	No. of results
H,H	1.3-' 2'	7
H,X	$1 \cdot 1 - 1 \cdot 5$	15
X,X	< 0.2	11

\* X is any organic substituent; X = Alk or Ar, or X,X = -(CH<sub>2</sub>)<sub>n</sub>-.

Chemical Shift  $\tau_{\rm b}$ .—In contrast,  $\tau_{\rm b}$  for the proton in the C=N-CHOR system shows few systematic trends, al-

\* There is a possible exception in the compound (Pr<sup>i</sup>CH:N)<sub>2</sub>CHPr<sup>i</sup>, but the results given <sup>13</sup> are not clear enough to establish the point and in any case this is an unusual system.

V. Bekárek, J. Kliknar, F. Kristek, and M. Večeřa, Coll. Czech. Chem. Comm., 1968, 33, 994.
 K. Tabei and E. Saitou, Bull. Chem. Soc. Japan, 1969, 42,

1440.

isomers (P trans to CHQR). Like Hine and Yeh we found no evidence in the spectra for the co-existence of the cis-isomers. The value of  $|J_{ab}|$  decreases in the series (Q,R) = (H,H), (H,X), (X,X), being undetectably small in the last case for all the examples studied.\* This is entirely consistent with the existence of discrete conformers of structure (II), obtained by rotation about the N-C(3) single bond, and having energy differences which are large enough to give strong preference to some of these conformations at room temperature. It seems likely <sup>5,14</sup> that the conformers all have one of the CHQR bonds eclipsed to the C=N double bond (*i.e.*  $\phi \simeq 0$ ) and the observed dependence of  $|J_{ab}|$  will then result. In the

<sup>12</sup> J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, Toronto, and London, 1959; J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Reson-ance Spectroscopy,' vol. II, Pergamon, Oxford, 1966. <sup>13</sup> R. H. Hasek, E. U. Elam, and J. C. Martin, J. Org. Chem., 1061 06 1829.

1961, **26**, 1822.

<sup>14</sup> J. T. Yardley, J. Hinze, and R. F. Curl, J. Chem. Phys., 1964, **41**, 2562.

case where Q, R = H, H there will always be two H<sup>b</sup> atoms with  $\phi$  near  $-30^{\circ}$  or  $+210^{\circ}$  and the strongest coupling results. When Q, R = H, X the conformation with X eclipsed to the C=N bond will be the least favoured, so there will most probably be only one H<sup>b</sup> atom with  $\phi$  near -30 or  $+210^{\circ}$  and the coupling is reduced. When Q, R = X, X, the lone H<sup>b</sup> atom will be

held preferentially in the eclipsed position and the resulting coupling constant is very small.

Thus the effects observed here for aldimines seem to be entirely analogous to those found in olefins. It should now be interesting to confirm these conclusions by more detailed studies on a few selected compounds.

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