auch unsere Honigbienen, so wie es heute noch ihre nächsten Verwandten, die indischen Bienen, tun, ihre Waben unter freiem Himmel gebaut haben. So mag auch für die Fourageure die Lage ursprünglich so gewesen sein wie heute noch für die Quartiermacher.

Man wird fragen, ob denn eine Richtungsangabe, die mit einer beträchtlichen «Missweisung» verbunden ist, für das Bienenvolk überhaupt einen Wert hat. Die Antwort lautet: die gewiesene Richtung erscheint nur uns falsch. Die benachrichtigten Bienen kompensieren die Abweichung bei der Rückübersetzung des Schwerkraftwinkels in den Sonnenwinkel und fliegen richtig. Das hat sich bei Fächerversuchen sowohl für die starke «Missweisung», von welcher hier die Rede war, wie auch für die kleinere «Restmissweisung» ergeben ([2], p. 585 und 589). Das bedeutet, dass die verschiedenen Bedingungen, die bei der Tänzerin für die «Missweisung» mitbestimmend sind – Anblick blauen Himmels, Art des Polarisationsmusters, Anblick der Sonne, Grad ihrer Verschleierung, Betrag der «Restmissweisung» und wohl noch anderes – von den Empfängern der Nachricht nach Sinn und Ausmass entsprechend in Rechnung gestellt werden. Ein Bienenvolk ist bei seiner uralten, auf Instinkte gegründeten Tradition – ganz anders als eine menschliche Gesellschaft – eine Versammlung gleichgestimmter Seelen, die auf die Art und Weise, wie sie angesprochen wird, einheitlich reagiert und einer individuellen Auslegung und freiwilligen Entscheidung wenig übrig lässt.

Summary. Bees are able to indicate direction to their hive comrades by means of a waggling dance of 2 kinds: in the horizontal plane with regard to the sun they point directly towards the goal by a waggling walk using the same angle to the sun as they took in their flight. Inside the dark hive in the vertical honey-comb, they transpose the angle between goal and sun to the field of gravity, whereby the sun's direction is shown by a waggling walk upwards, and the angle to the right or left of the sun's position is given by a dance-direction in the corresponding angle to the right or left of the zenith.

If a piece of blue sky is made visible in an observation hive to the bees which are dancing in orientation by gravity, they recognise the position of the sun by this polarisation sample, and the effort to orientate themselves directly by the sun (as in the horizontal plane) comes into conflict with the orientation by gravity. The result is a dance direction which corresponds remarkably well with the halving of the angle between what the dance direction should have been by gravity and what it should have been by light orientation (Figure 1). This is also true when the bee is orientating itself by polarised sky light over its back, while the sun is at the other side of the honey-comb under its front (Figure 2), a situation which does not occur during flight but which is important for its dance in the swarm. The bees receiving the information compensate the deviation of the angle determined by light, and fly to the right goal.

As the sun itself, as well as the piece of blue sky, was made visible to the dancers, its influence dominated and they orientated themselves by its light (Figure 3).

Brèves communications – Kurze Mitteilungen – Brevi comunicazioni – Brief Reports

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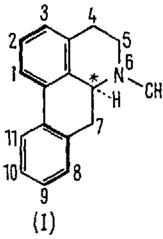
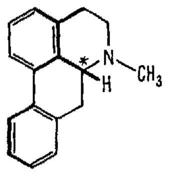
Optical Rotatory Dispersion Studies[1]. Configurational Assignments among the Aporphine Alkaloids

The aporphines represent a large group of alkaloids[2] based on the skeleton I (or its antipode II). The absolute configuration of several members of this class was first considered by Bentley and Cardwell[3] in terms of the α or β orientation of the hydrogen atom attached to the single asymmetric carbon (starred in I and II). In actual fact, the aporphine skeleton also represents a permanently twisted biphenyl system and, as has been pointed out recently[4], the chirality of this twisted biphenyl is uniquely determined by the absolute configuration of the asymmetric carbon atom. In terms of the Cahn-Ingold-Prelog convention[5], the biphenyl system of I belongs to the (S)-series, while the (R)-notation must be attributed to the



(I)



(II)

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[1] Paper LXII; paper LXI see C. Djerassi, J. Fishman, and T. Nambara, Exper. *17*, 565 (1961).

[2] For pertinent references see R. H. F. Manske, *The Alkaloids* (Academic Press, New York 1954), vol. IV, chapter 30. – T. A. Henry, *The Plant Alkaloids* (Blakiston, Philadelphia 1949), p. 306.

[3] K. W. Bentley and H. M. E. Cardwell, J. chem. Soc. *1955*, 3252.

[4] M. Shamma, Exper. *16*, 484 (1960).

[5] R. S. Cahn, C. K. Ingold, and V. Prelog, Exper. *12*, 81 (1956).

antipode II. This emphasis upon the biphenyl moiety is important for our subsequent rotatory dispersion discussion, since the relevant absorption bands are all associated with this aromatic portion of the molecule.

All of the naturally occurring aporphines possess oxygenated (hydroxyl, methoxyl, methylenedioxy) substituents at positions 1 and 2, while the other aromatic ring may or may not have such a group at position 11. As noted in an earlier paper[4], the presence of a C-11 substituent manifests itself by rather high specific rotations (at the sodium D line) and an ultraviolet absorption maximum near 270 mμ, while the C-11 unsubstituted members show much lower rotations as well as a bathochromic shift to 282 mμ. In addition, the spectra of both groups contain a maximum in the 300 mμ region. These are then the absorption bands which are of principal concern to us.

(+)-Bulbocapnine (III) may be considered as the configurational reference standard of the C-11 substituted aporphines. Its absolute configuration is established by its conversion[6] into (+)-morphothebaine, which is the antipode of (−)-morphothebaine of known absolute configuration[7]. Conversely, (+)-glaucine (IV) may be taken as the prototype of the 11-unsubstituted aporphines and its absolute configuration has been established rigorously[8] through its relationship[9] to laudanosine (of same sign of rotation). Consequently, both (+)-bulbocapnine (III) and (+)-glaucine (IV) belong to the biphenyl system I and this applies also to (+)-boldine (V), (+)-dicentrine (VI), (+)-glaucentrine and (+)-laurotetanine, all of which have been interrelated[2] with IV[10].

BENTLEY and **CARDWELL**[3] noted that all of the above aporphine alkaloids were dextrorotatory at the sodium D line and thence generalized that this could be used as a criterion for assigning absolute configurations. In view of the potential danger of utilizing monochromatic rotations as compared to rotatory dispersion curves[11] for such configurational interrelations, we decided to measure the rotatory dispersion curves of several aporphines of known as well as unknown absolute configuration. Such a study became particularly pertinent, because of the extensive rotatory dispersion measurements and subsequent stereochemical generalizations which have been performed recently among twisted biphenyls[12].

We shall start out with the well-known fact that the twisted biphenyl chromophore (as in I or II) not only contributes to optical activity[13], but that in particular it will play a very important role in any Cotton effects that may be observed in the rotatory dispersion curves of aporphines. Secondly, it must be pointed out that the presence of a C-11 substituent (e.g. III *vs.* IV) may result in out of plane bending of the C-1 and C-11 groups as well as in a distortion of bond and torsion angles in the aporphine framework[14,15]. With this information as background, we may consider the optical rotatory dispersion curves of the various aporphines both in terms of relevant optically active absorption bands and in terms of absolute configuration. Because of the rather high absorption (ε *ca.* 10000) near 300 mμ, most of the ultraviolet rotatory dispersion measurements had to be conducted in very dilute solution and therefore are subject to a fairly large error in that region. However, from a qualitative standpoint, the results (to 320 mμ) are completely reliable, and this was checked with 'blank' measurements on racemic aporphines, which did not give rise to false rotations associated with stray light[16].

Even a cursory inspection of Figure 1–4 will show immediately that a coincidence in sign of the sodium D line rotation, as employed by **BENTLEY** and **CARDWELL**[3],

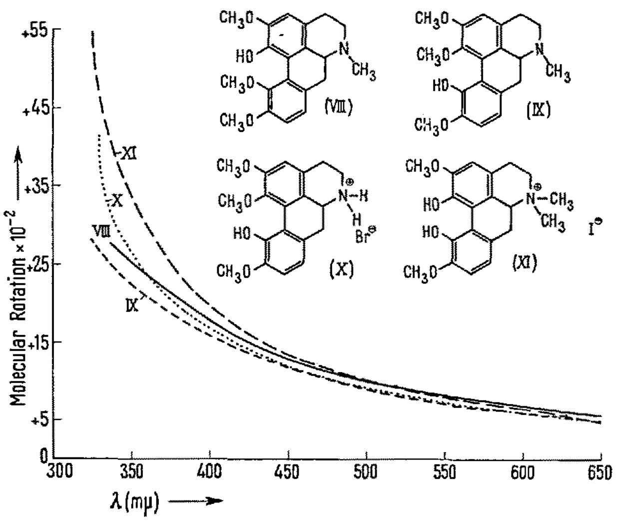

Fig. 1. Rotatory dispersion curves of corydine (VIII), isocorydine (IX), norisocorydine hydrobromide (X), and magnoflorine iodide (XI) in methanol.

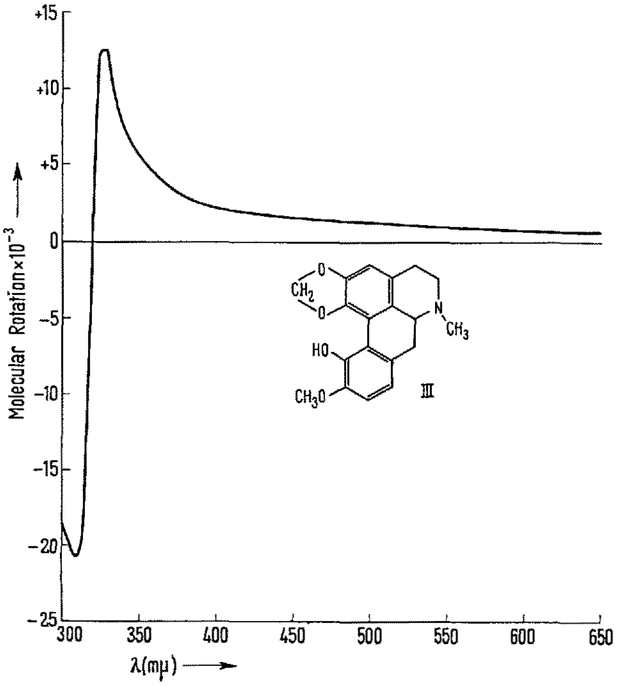

Fig. 2. Rotatory dispersion curve of bulbocapnine (III) in methanol.

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[6] W. A. AYER and W. I. TAYLOR, J. chem. Soc. *1956*, 472, and footnote 15 in ref. [8].

[7] J. KALVODA, P. BUCHSCHACHER, and O. JEGER, Helv. chim. Acta *38*, 1847 (1955).

[8] H. CORRODI and E. HARDEGGER, Helv. chim. Acta *39*, 889 (1956).

[9] F. FALTIS and E. ADLER, Arch. Pharm. *284*, 281 (1951).

[10] The statement (ref. [3]) that (+)-domesticine has been related chemically to (+)-glaucine is not correct.

[11] C. DJERASSI, *Optical Rotatory Dispersion* (McGraw-Hill, New York 1960), especially chapters 10 and 16.

[12] K. MISLOW, M. A. W. GLASS, R. E. O'BRIEN, P. RUTKIN, D. H. STEINBERG, and C. DJERASSI, J. Amer. chem. Soc. *82*, 4740 (1960); J. Amer. chem. Soc., in press.

[13] K. MISLOW, Angew. Chem. *70*, 683 (1958), and leading references listed therein.

[14] G. H. BEAVEN, D. M. HALL, M. S. LESSLIE, and E. E. TURNER, J. chem. Soc. *1952*, 854.

[15] R. PEPINSKI, Y. OKAYA, and T. ASHIDA, forthcoming publication.

[16] C. DJERASSI, E. LUND, E. BUNNENBERG, and J. C. SHEEHAN, J. org. Chem. *26*, in press (1961).

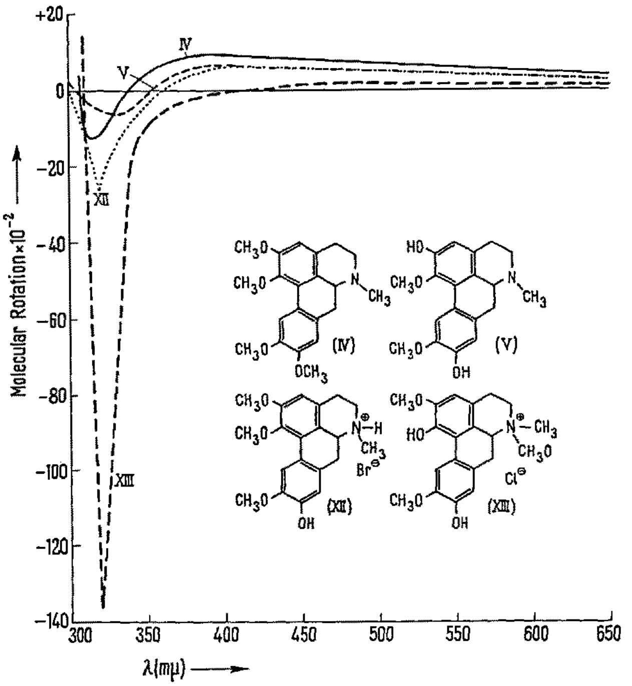

Fig. 3. Rotatory dispersion curves of glaucine (IV), boldine (V), N-methyllaurotetanine hydrobromide (XII), and laurifoline chloride (XIII) in methanol.

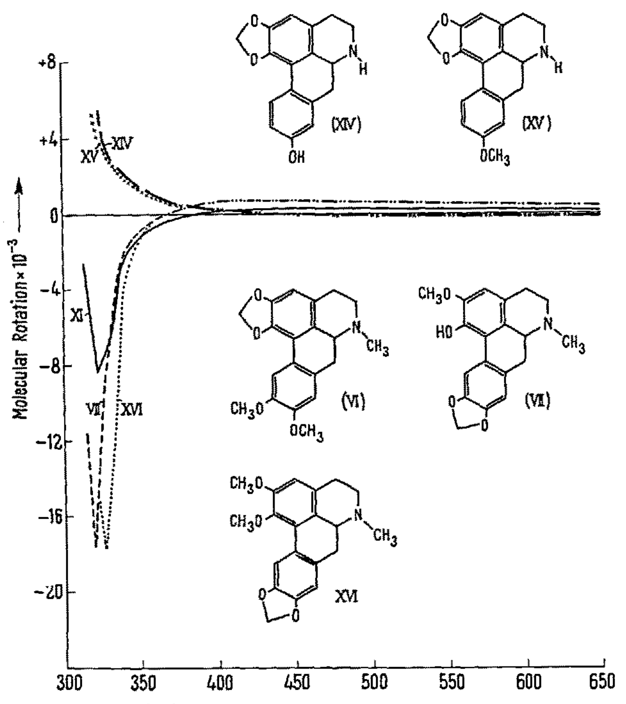

Fig. 4. Rotatory dispersion curves of dicentrine (VI), domesticine (VII), nantenine (XVI), anolobine (XIV), and xylopine (XV) in methanol.

does not necessarily reflect the sign of the long-wavelength Cotton effect. On the basis of the structural and absolute configurational information now at hand (see above discussion), we feel justified to make the following two empirical generalizations concerning the optical rotatory behavior of the various aporphines.

(1) The presence of a methylenedioxy substituent significantly enhances the amplitude of the long-wavelength Cotton effect curve (e.g. bulbocapnine, domesticine, dicentrine, xylopine, analobine; Figure 2, 4), without significantly changing the respective ultraviolet spectra. However, since systems which do not contain the methylenedioxy substituent may also on occasion exhibit enhanced amplitudes (e.g. laurifoline chloride), this particular feature of the rotatory dispersion curve may not safely be used in assignments of the methylenedioxy function.

(2) All of the C-11 unsubstituted aporphines at our disposal carried at the same time an oxygen function at C-9. The change from the 1, 2, 10, 11-tetrasubstitution pattern (Figure 1, 2) to the 1, 2, 9, 10-tetra-oxygenated aporphines (Figure 3, 4) is accompanied by (a) incursion of a background curve of opposite sign to that of the long-wavelength Cotton effect and (b) the reversal of the sign of the long-wavelength Cotton effect.

We shall now discuss the basis for the structural and configurational conclusions that may be derived from these rotatory dispersion data. Thus, domesticine (VII), which has not been related chemically[10] to one of the absolute configurational standards, may confidently be assigned the same absolute configuration (I) as (+)-dicentrine (VI). All the alkaloids in Figure 3 have such similar rotatory dispersion curves that a common absolute configuration must follow, in accord with chemical evidence[2]. The same stereochemical identity can be inferred for the alkaloids whose rotatory dispersion curves are collected in Figure 1.

The incursion of the above mentioned background rotation (of opposite sign) is clearly linked to the bathochromic shift of the band near 270 mμ to 282 mμ, which has been noticed[4] to accompany the removal of the C-11 substituent. Since the absolute configurations of dicentrine and the alkaloids in Figure 3 are firmly established (*via* glaucine[8]) and since the ultraviolet absorption spectra of all these substances are virtually identical, we conclude that a ***negative*** Cotton effect curve (overlapped by the tail of a positive background curve presumably centered at shorter wavelength) identifies absolute configuration I for *that particular 1, 2, 9, 10-substitution pattern*.

Turning to the alkaloids in Figure 1 and 2, whose ultraviolet spectra are superimposable, we feel justified in postulating that a ***positive*** Cotton effect *curve with no apparent background* (corresponding to the 270 mμ alkoxyphenyl bands) corresponds to configuration I, this generalization applying to the *1, 2, 10, 11-substituent pattern*. With the absolute configuration of (+)-bulbocapnine (III) established[6,15], we thus regard the absolute configurational problem in the corydine group (isocorydine and norcorydine) as solved.

The above limitations to certain substitution patterns are justified in the light of our earlier findings[12] that the rotatory dispersion behaviour in the twisted biphenyl series is extraordinarily sensitive to alterations in the position of substituents in the biphenyl nucleus.

Assuming that the sign of the background curve in domesticine (VII), dicentrine (VI) and the alkaloids of Figure 3 is correctly associated with the 282 mμ band, the opposite absolute configurations (II) may be assigned to anolobine (XIV) and xylopine (XV), which share with the afore-mentioned alkaloids the substitution at C-9 (and absence of substitution at C-11) as well as the band at 282 mμ, even though the longer-wavelength features of the absorption spectrum differ appreciably. This represents another instance of the advantage of rotatory dispersion over monochromatic rotational measurements as BENT-

LEY and CARDWELL[3] were not able to utilize the relatively low D line rotation of anolobine (XIV) for a configurational assignment. However, it should be pointed out that so far rotatory dispersion measurements bear out their assumption[3] that a positive D line rotation is associated with absolute configuration I. We shall refrain from attempting to correlate at this time the rotatory dispersion behavior of the presently discussed aporphines and the previously investigated[12] elagitannin-derived polyalkoxy-biphenyls, since we are aware of the complexity in the relationship of rotatory dispersions and stereochemistry in these structural types[17].

Résumé. Les configurations absolues de certains alkaloïdes de l'aporphine ont été détérminées à partir de leurs courbes de dispersion rotatoire.

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Department of Chemistry, Stanford University, Stanford (Calif.), Department of Chemistry, New York University, New York, and Department of Chemistry, The Pennsylvania State University, University Park (Penn. USA), September 25, 1961.

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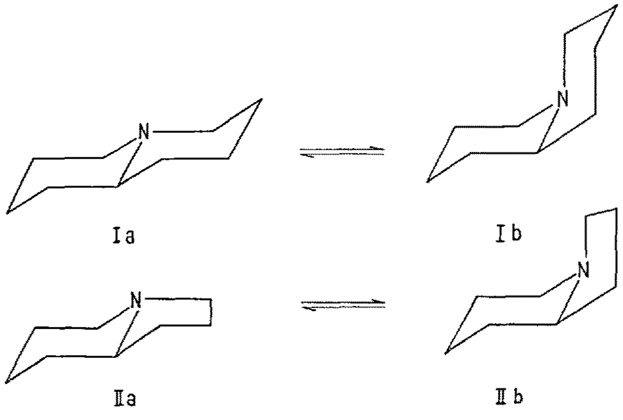
The Stereochemistry of Quinolizidine and Octahydropyrocoline

In quinolizidine and octahydropyrocoline, due to easy inversion of the nitrogen atom, the energy barrier between *cis* and *trans*-fused forms[1] is low, and they may be termed as conformations. Conformational arguments attributing greater stability to the *trans*-fused forms (Ia and IIa) have been put forward by analogy with decalin and hydrindane systems[2–5]. However, if the findings of ARONEY and LE FEVRE[6] (the volume requirements of a nitrogen lone pair exceed those of hydrogen and approach the methyl group) are taken into consideration, these bases are more likely to resemble the corresponding carbocyclic systems with an angular methyl group.



Assigning, to the lone pair of the bridgehead nitrogen, an angular effect[7] of 0.8 kcal/*M* in favour of *cis*-fusion, we have estimated the enthalpy of the conversion Ib $\rightleftharpoons$ Ia to be roughly -1.9 kcal/*M*. For octahydropyrocoline the enthalpy of conversion IIb $\rightleftharpoons$ IIa comes to be -0.3 kcal/M. It is assumed that the replacement of carbon by nitrogen does not alter the geometry and consequently the thermodynamic constants for the corresponding carbocyclic systems[8] have been used in these estimations. The equilibrium, in the latter case at least, should lie further in favour of the *cis*-fused conformation, due to its greater entropy. This entropy effect may, however, be less prominent when bigger fused systems like E/F ring of solanidane nucleus are considered[9].

Several naturally occurring bases with these systems have substituents whose position (axial or equatorial) alters with the *cis* $\rightleftharpoons$ *trans* conversion, and this should be taken into consideration when predicting the position of the equilibrium. In cevine[10] ring E/F, for example, the C-25 methyl group is axial in the *trans* (IIIa) and equitorial in the *cis*-fused (IIIb) conformation. Using a destabilisation value of 2.4 kcal/*M*[11] for putting an axial methyl group *cis* to the nitrogen lone pair, the *cis*-fused conformation comes to be more stable by 0.5 kcal/*M*. In the case of lupinine[2], however, hydrogen bonding which is possible only in the *trans*-fused (IVa) conformation may shift the equilibrium in its favour.

BOHLMANN[3] has demonstrated that *trans*-fused quinolizidines, in which the nitrogen lone pair is *trans* to at least two axial hydrogen atoms on carbon adjacent to it, show a prominent band in the 2800–2700 cm^{-1} region. This criterion has often been used to assign *trans*-fused conformations to such systems[3–5,12]. Further MOYNEHAN et al.[5], on the basis of I.R. and N.M.R. evidence, have

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[1] In systems where one of the rings is frozen only one of the two possible *cis* isomers (with N–C bond axial with respect to the frozen ring) is easily convertible to the *trans* form.

[2] R. C. COOKSON, Chem. and Ind. *1953*, 337. It is suggested that compared to decalin the *cis trans* energy difference may be greater in quinolizidine because it has one less angular hydrogen.

[3] F. BOHLMANN, Chem. Ber. *91*, 2157 (1958).

[4] N. J. LEONARD and W. K. MUSKER, J. Amer. chem. Soc. *82*, 5148 (1960).

[5] T. M. MOYNEHAN et al., Proc. chem. Soc. *1961*, 218.

[6] M. ARONEY and R. J. W. LE FEVRE, Proc. chem. Soc. *1958*, 82; J. chem. Soc. *1958*, 3002; J. chem. Soc. *1960*, 2161. See also D. H. R. BARTON and R. C. COOKSON, Quart. Rev. *10*, 44 (1956).

[7] The 0.8 kcal/*M* value is arbitrarily chosen on the assumption that the effect of nitrogen lone pair is half that of the angular methyl group ($^1/_2$ × two 0.8 kcal/*M* skew interactions).

[8] N. L. ALLINGER and J. L. COKE, J. Amer. chem. Soc. *81*, 4080 (1959); *cis* decalin $\rightleftharpoons$ *trans* decalin, $\Delta H = -2.7$ kcal/*M*; J. Amer. chem. Soc. *82*, 2553 (1960), *cis* hydrindane $\rightleftharpoons$ *trans* hydrindane, $\Delta H = -1.1$ kcal/*M*.

[9] N. L. ALLINGER, J. org. Chem. *21*, 915 (1956).

[10] S. M. KUPCHAN, W. S. JOHNSON, and S. RAJAGOPALAN, Tetrahedron *7*, 47 (1959).

[11] The 2.4 kcal/*M* value is arbitrarily chosen, 1.6 kcal/*M* for axial methyl and 0.8 kcal/*M* additional for its being *cis* to the nitrogen lone pair.

[12] Y. SATO and N. IKEKAWA, J. org. Chem. *26*, 1945 (1961).