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The Rotation–Inversion Dichotomy in Trialkylamines. Direct ^{1}H DNMR Observation of Distinctly Different Rates of Nitrogen Inversion and Carbon–Nitrogen Bond Rotation in Isopropylmethylethylamine

C. Hackett Bushweller,*[1a,2] Chih Y. Wang,[1b] Jean Reny,[1b] and Marilyn Z. Lourandos[1b]

Contribution from the Departments of Chemistry, State University of New York at Albany, Albany, New York 12222, and Worcester Polytechnic Institute, Worcester, Massachusetts 01609. *Received November 1, 1976*

Abstract: Examination of the ^{1}H[^{2}H] DNMR spectrum of (isopropyl-2-*d*)(methyl-d_3)(ethyl-2,2,2-d_3)amine in $CBrF_3$ reveals for the first time in an acyclic trialkylamine two distinctly different coalescence phenomena one of which can be assigned to nitrogen *inversion* ($\Delta H^{\ddagger} = 8.3 \pm 0.5$ kcal/mol; $\Delta S^{\ddagger} = 5.5 \pm 4.0$ gibbs; $\Delta G^{\ddagger} = 7.5 \pm 0.2$ kcal/mol at -121.3 °C) and the other to C–N bond *rotation* ($\Delta H^{\ddagger} = 5.3 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -3 \pm 2$ gibbs; $\Delta G^{\ddagger} = 5.6 \pm 0.2$ kcal/mol at -157.8 °C).

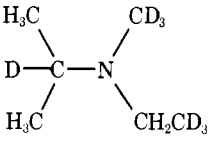
In a recent paper concerning *hindered N-tert*-butyl-*N,N*-dialkylamines, we presented evidence for a stereodynamical itinerary which *couples tert*-butyl rotation and nitrogen inversion.[3] Indeed, it is this pathway that provides the lowest barrier route for equilibrating the *tert*-butyl methyl groups as well as inverting the nitrogen atom. The implication in this dynamical model is that the barrier to isolated *tert*-butyl rotation with *no* concomitant inversion at nitrogen is *higher* than that for the coupled inversion–rotation process.[3] Since the DNMR method is sensitive only to the lowest barrier itinerary of several pathways by which the same net conformational exchange may occur, isolated *tert*-butyl rotation in the hindered *N-tert*-butyl-*N,N*-dialkylamines is invisible to the DNMR technique. This situation precludes the observation of two separate DNMR coalescence phenomena over different respective temperature ranges due to nitrogen inversion in one case and isolated *tert*-butyl rotation in the other. In *less hindered* trialkylamines such as methylamine, dimethylamine, and trimethylamine, theoretical calculations[3] and experimental measurements[4] indicate that the barrier to isolated C–N rotation is consistently *lower* than that for inversion. However, in all of the reported DNMR investigations of less hindered acyclic trialkylamines such as dibenzylmethylamine,[3,5] examination of the ^{1}H DNMR spectra of pertinent diastereotopic groups revealed changes consistent with slowing only nitrogen inversion. Separate DNMR coalescence phenomena attributable to nitrogen inversion in one instance and isolated C–N rotation in the other have not been observed. In these *less hindered* trialkylamines, this situation is due most likely to barriers for C–N rotation which are below the lower limit of DNMR detection (~4 kcal/mol).

We also presented data for a series of *N-tert*-butyl-*N*-chloramines indicating that an electronegative N-substituent such as chlorine effectively *decouples tert*-butyl rotation from nitrogen inversion by *raising* the barrier to inversion relative to isolated *tert*-butyl rotation.[6] In this instance, two separate DNMR coalescence phenomena due to inversion and *tert*-butyl rotation are observed over two different temperature ranges.

This report concerns what we believe to be the first direct observation for an *acyclic trialkylamine* of two separate and distinct ^{1}H DNMR coalescence phenomena one of which can be ascribed to nitrogen *inversion* and the other to C–N bond *rotation*.

Results and Discussion

Examination of the ^{1}H[^{2}H] DNMR spectrum (60 MHz) of **1** (5% v/v in $CBrF_3$; Figure 1) at -65.4 °C shows two singlet



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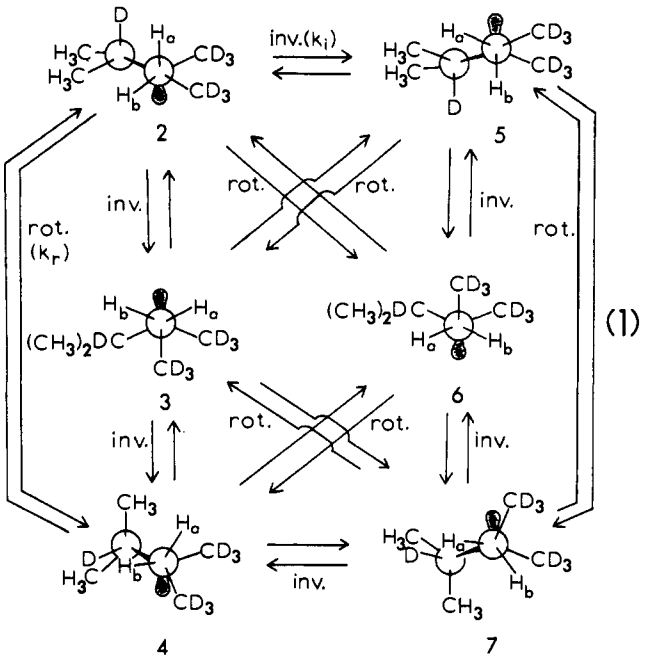
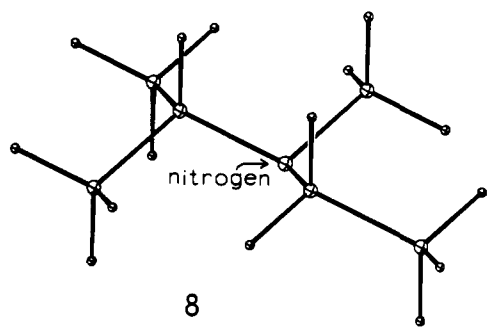
resonances at δ 0.98 [6 H, $(CH_3)_2CD$] and δ 2.37 [2 H, CH_2]. At lower temperatures (Figure 1), each of these two resonances undergoes two separate and clearly defined coalescence phenomena. At -140.3 °C (Figure 1), the CH_2 resonance consists of *one* AB spectrum albeit distorted while the $(CH_3)_2CD$ resonance is separated into two singlets. The spectral changes for the CH_2 group can be rationalized with the aid of eq 1 (projection down H_2C–N bond) and the results of theoretical calculations performed in our laboratory.

Using standard bond lengths (C–N, 1.47 Å; C–C, 1.54 Å; C–H, 1.09 Å) and all methyl groups essentially perfectly staggered, a geometry optimization approach using the INDO-A method[7] led to the prediction of four stable conformations, i.e., two pairs of enantiomers. One enantiomer from each pair is illustrated respectively in structures **8** and **9** for nondeuterated **1**. Conformer **8** is calculated to be 0.18 kcal/mol more stable than **9** with both **8** and **9** having optimized CNC bond angles of 113.1°. In **8**, the lone pair is gauche to the two isopropyl methyl groups with a dihedral angle of 159° between the central isopropyl C–H bond and the lone pair (methine hydrogen leaning toward the ethyl group). In **9**, the dihedral angle between the CH_2CH_3 carbon–carbon bond and the lone pair is 10° with an essentially flat potential minimum for di-



(1)



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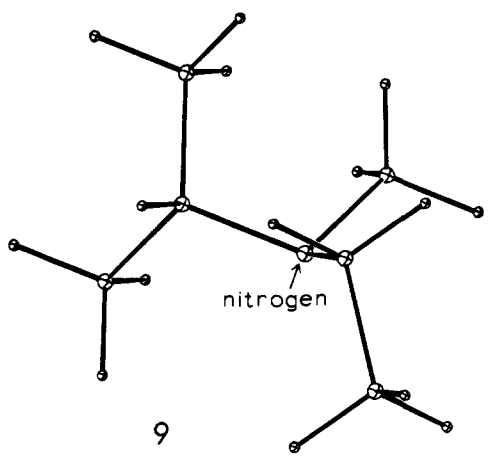

9

hedral angles from 60 to 90° between the central isopropyl C–H bond and the lone pair (methine hydrogen toward ethyl). Modifications of **9** with dihedral angles between the ethyl carbon–carbon bond and the lone pair of 0 and 350° are respectively 0.008 and 0.08 kcal/mol less stable than **9**. It is apparent that both the isopropyl and ethyl groups may undergo facile wagging motions in a geometry such as **9**. *It should be noted at this point that conversion of* **8** *to* **9** *requires rotation of both the ethyl and isopropyl groups.* Conformations such as **3** or **6** (eq 1) which involve a gauche orientation of the methyl group of ethyl with respect to the *N*-methyl or *N*-isopropyl groups are calculated to be at least 1.2 kcal/mol higher in energy than **8** or **9**. In eq 1, **2** is then a representation of the selectively deuterated derivative of **8**; **4** (eq 1) corresponds to **9**.

These theoretical calculations then indicate that **1** exists as *four stable conformations*, i.e., **2**, **4**, and their respective enantiomers **5** and **7** (eq 1). The presence of just four dominant species for **1** is crucial to our analysis of the DNMR spectra (Figure 1) discussed below.

In eq 1, the *direct* interconversions **2** to **3**, **3** to **4**, **4** to **7**, **7** to **6**, **6** to **5**, **5** to **2**, and each respective reverse process involve *inversion* at nitrogen *and* a required *rotation* of both ethyl and isopropyl groups. For example, conversion of **2** to **5** requires inversion at nitrogen *and* a 60° counterclockwise rotation about the N–CH_2 bond. For the **2** to **5** process, inversion is also accompanied by a 138° rotation of isopropyl. For the **2** to **3** to **4** double inversion process, ethyl undergoes a net 50° clockwise rotation and isopropyl an approximate 85° rotation. As revealed in our previous papers,[3,5] C–N rotation is an extremely facile process as nitrogen approaches sp^2 hybridization in the transition state for inversion. It is very reasonable to expect that such rotational reorientations associated with the **2** to **5** or **2** to **3** to **4** processes will occur very efficiently in the course of nitrogen inversion. Such concerted inversion–rotation processes are labeled inv. in eq 1 with the associated first-order rate constant designated as k_i. In eq 1, the direct interconversions **2** to **4**, **4** to **6**, **6** to **2**, **5** to **3**, **3** to **7**, **7** to **5**, and each respective reverse process involve *rotation* (eq 1; rot.; k_r) about C–N bonds against a nitrogen atom which is fixed in a pyramidal geometry. *Direct conversion of* **2** *to* **4** *or* **5** *to* **7** *involves not only rotation of the ethyl group but also rotation of isopropyl.* Under conditions of *slow inversion*, two isolated sets of *stable* rotational isomers exist (**2** and **4**; **5** and **7**). Thus, assuming that conformers such as **3** and **6** are present in too low a concentration to affect the DNMR spectrum to any appreciable degree, and thereby assuming the presence of four stable conformers, i.e., two pairs of enantiomers (eq 1; **2** and **5**, **4** and **7**), a standard rationale[3,5,6] for the behavior of the CH_2 resonance (eq 1) states that under conditions of *slow inversion* (eq 1; **2** to **5**, **4** to **7**, **2** to **3** to **4**, **5** to **6** to **7**, etc.) and *fast C–N rotation* (eq 1; **2** to **4**, **5** to **7**, etc.) the CH_2 resonance should be a *single AB spectrum.* Since the methylene group experiences an asymmetric nitrogen atom, rapid C–N rotation alone will not swap the environments of H_a and H_b (eq 1). Thus, if inversion is slow and all C–N rotations are rapid, a single AB spectrum is observed resulting from the superposition of two identical AB spectra one from each of the two sets of rotational isomers. Indeed, this is the case at −140.3 °C although the AB spectrum is distorted by the initial onset of slowing a second rate process (Figure 1).

If inversion were rapid and rotation were slow, the methylene resonance would remain a singlet because inversion does indeed still provide a mechanism for swapping the environments of H_a and H_b (see eq 1).

The assumption in this rationale is that the barriers to inversion for the processes **2** to **5** and **4** to **7** are very similar. Conformers **3** and **6** are assumed to be unstable intermediates. Since the bulk of the energy change in the inversion process involves rehybridizing nitrogen,[3,6] the inversion barrier from **2** to the unstable **3** or from **5** to the unstable **6** should be similar to the **2** to **5** or **4** to **7** processes. Thus, it is apparent that the observation of a single AB spectrum at −140.3 °C (Figure 1) is consistent with C–N rotation (**2** to **4**, **5** to **7**; eq 1) having a lower barrier than inversion and that C–N rotation is rapid relative to inversion on the DNMR time scale at −140.3 °C. The double inversion processes (**2** to **3** to **4**; **5** to **6** to **7**) are presumably slow at −140.3 °C and do not contribute significantly to exchange between **2** and **4** or **5** and **7** due to the more rapid rotation processes.

A similar rationale may be applied to the isopropyl doublet at −140.3 °C (Figure 1). Thus, the diastereotopic methylene

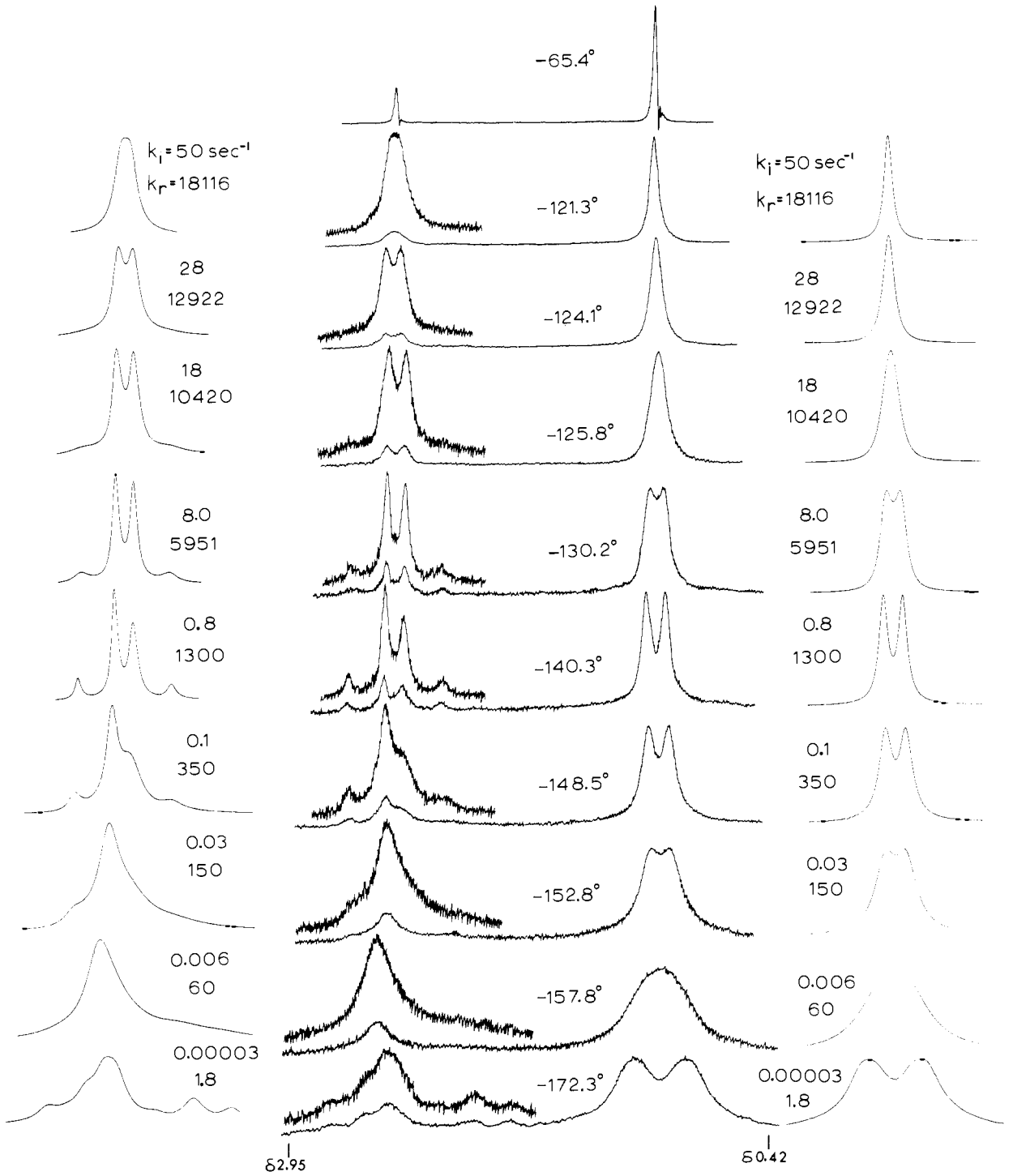

Figure 1. The experimental $^1H[^2H]$ DNMR spectra (60 MHz) of the methylene and isopropyl resonances of **1** (5% v/v in $CBrF_3$) as a function of temperature and theoretical spectra generated as a function of the rate of inversion (k_i; eq 1: **2** to **5**, **4** to **7**) and C–N rotation (k_r; eq 1: **2** to **4**, **5** to **7**).

and isopropyl groups of **1** provide a unique double probe for the inversion process in **1**.

Obviously, if C–N rotation then slows down on the DNMR time scale under conditions of static inversion, the ^1H DNMR spectrum for the methylene protons should separate into two AB spectra one for enantiomers **2** and **5** and the other for enantiomers **4** and **7**. Conformers **3** and **6** would presumably be too unstable to be detected. At temperatures below −140.3 °C (Figure 1), additional simultaneous changes in both the methylene and isopropyl resonances do indeed occur revealing the slowing of C–N rotation on the DNMR time scale. At −172.3 °C (Figure 1), a complete ^1H DNMR line shape analysis is consistent with the presence of two superimposed AB spectra (δ 2.66, 1.91 (J_{AB} = −12 Hz) and 2.53, 2.35 (J_{AB} = −12 Hz) respective relative populations of 0.46 and 0.54). The slow exchange methylene spectrum at −172.3 °C is best rationalized in terms of slow C–N rotation (e.g., **2** to **4**, **5** to **7**; eq 1) with a noninverting nitrogen. Thus, under conditions of slow inversion and slow rotation, the presence of two different pairs of enantiomers (**2** and **5**, **4** and **7**; eq 1) will lead to two different AB spectra as observed. Based on the established significant upfield shift of a proton which is trans to the nitrogen lone pair[8] (e.g., H_a in **2** or H_b in **5**), the AB spectrum having the larger AB chemical shift difference may be assigned to **2** and **5** (eq 1; also see structure **8**). No such trans relationship exists for H_a or H_b in **4** or **7** (eq 1; also see structure **9**).

Consistent with the above interpretation, the isopropyl resonance at −172.3 °C is accurately simulated using two superimposed doublet resonances one at δ 1.16 and 0.80 and the other at δ 1.08 and 0.88 with respective relative populations of 0.46 and 0.54.

It is obvious of course that *rotation* of **2** to **4** or **5** to **7** involves C–N rotation for *both* the ethyl and isopropyl groups. Only one of these processes need have a barrier within the limits of the DNMR method to produce the observed spectral changes (Figure 1). Based on steric arguments only, the rate-controlling process is most likely isopropyl C–N rotation with the ethyl group rotating in concert with the isopropyl group or in a separate rotation (after isopropyl rotation) to the appropriate optimized geometry. The nature of the DNMR spectra do not allow a stereodynamical distinction between ethyl or isopropyl rotation being rate-controlling. *However, it is clear that although multiple in character, C–N rotation has been observed under conditions of static nitrogen inversion in an acyclic trialkylamine.*

Complete ^{1}H DNMR line shape analyses for both the methylene and isopropyl resonances were performed using a locally revised version of computer program DNMR3[9] and employing four molecular configurations (eq 1: **2, 4, 5, 7**). The exact correlation between the k_i or k_r values (Figure 1) used separately for the methylene and isopropyl resonances speaks strongly for the stereodynamical model described above. Rate constants in Figure 1 which are either very large (>10 000) or very small (<0.5) have been extrapolated from values obtained for a particular rate process in the intermediate exchange region. Activation parameters for nitrogen inversion are $\Delta H^{\ddagger} = 8.3 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = 5.5 \pm 4.0$ gibbs, and $\Delta G^{\ddagger} = 7.5 \pm 0.2$ kcal/mol at −121.3 °C. For C–N rotation, they are $\Delta H^{\ddagger} = 5.3 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -3 \pm 2$ gibbs, and $\Delta G^{\ddagger} = 5.6 \pm 0.2$ kcal/mol at −157.8 °C.

It should be pointed out that in a formal sense separate DNMR coalescence phenomena for rotation and inversion have been observed in the *cyclic* system *N,N′,N″*-trimethyl-1,3,5-triazane[8] in which the barrier to ring reversal is observed to be much higher than that for nitrogen inversion. The ring reversal process does indeed involve rotation about C–N bonds but the transition state for ring reversal possesses a significant amount of angle strain which is not present in an acyclic case such as **1**.

The results reported here reveal that it is possible to observe separate and distinct DNMR coalescence phenomena for inversion and rotation rate processes in relatively unhindered acyclic trialkylamines and we are pursuing research aimed at assessing the effect of structural modifications on the relative rates of the two processes.

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Electronic States of Organic Molecules. 4. Ultraviolet Spectrum of Bicyclobutane[1]

Kenneth B. Wiberg,* G. Barney Ellison,[2] and Kevin S. Peters[3]

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received August 9, 1976*

Abstract: The ultraviolet spectrum of bicyclo[1.1.0]butane has been examined from 43 000 to 77 000 cm^{-1}. The first band (~45 000 cm^{-1}) is low in intensity, but has marked vibronic structure. The second band (~50 000 cm^{-1}) is broad, relatively intense, and has little structure. It probably results from a transition between the bonding and antibonding "π-like" central C-C bond orbitals. Another weak band (~58 000 cm^{-1}) follows which has a vibronic structure quite similar to that found in the first band. The remainder of the spectrum is relatively broad with little structure.

Bicyclo[1.1.0]butane, cyclobutene, and butadiene form an interesting triad of molecules which may be interconverted. Thermolysis of the first two leads to butadiene,[4] whereas irradiation of butadiene leads to both bicyclobutane and cyclobutene.[5] Our interest in these compounds and their interconversions has led us to examine their spectra in some detail. We have presented a vibrational analysis for the ground state of bicyclobutane,[6] and we now report the ultraviolet spectrum from 43 000 to 76 000 cm^{-1}. The spectra have been obtained for bicyclobutane-d_0, *-1,3-*d_2, and *-2,2,4,4-*d_4. The preparation of the labeled compounds has been given previously.[6]

Results

The ultraviolet spectrum of bicyclobutane-d_0 (H6) from 43 000 to 76 000 cm^{-1} is shown in Figures 1–4 and in Table I. The spectra of bicyclobutane-d_2 and -d_4 are similar. The lowest energy transition, Figure 2a, extends from 44 000 to 48 100 cm^{-1} and is not included in Figure 1. It is characterized