

Solvent Dependence of Primary Deuterium Kinetic Isotope Effects for Base-Catalyzed 1,3-Proton Transfer in the Indene System

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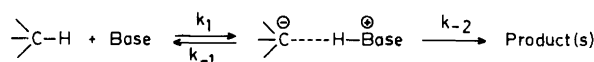
Hussénius, A. and Matsson, O., 1990. Solvent Dependence of Primary Deuterium Kinetic Isotope Effects for Base-Catalyzed 1,3-Proton Transfer in the Indene System. – Acta Chem. Scand. 44: 845–850.

Rate constants and primary deuterium kinetic isotope effects (KIEs) have been determined for the base-catalyzed 1,3-prototropic rearrangement of 1-methylindene and 1,3-dimethylindene in the solvents toluene, *o*-dichlorobenzene and dimethyl sulfoxide at 20 °C. The tertiary amines 1,4-diazabicyclo[2.2.2]octane (DABCO) and quinuclidine were used as catalysts. The variations in KIE for the two substrates are similar for both bases in all three solvent used, although the absolute values are lower for 1,3-dimethylindene. The total observed KIE range is from 5.03 to 7.83 for 1-methylindene and from 3.93 to 6.63 for 1,3-dimethylindene. For both substrates a pronounced solvent dependence of the KIE is observed, with an increase in the KIE with increasing solvent polarity. The results can be rationalized in terms of the Hammond postulate as a shift of transition state structure toward higher symmetry in the more polar solvents. The results are also in agreement with theoretical predictions based on the quantum-statistical mechanical model for hydron transfer reactions.

The magnitude of a primary deuterium kinetic isotope effect (KIE) for a proton transfer reaction is related to the overall free energy change for the reaction.¹ According to the Melander–Westheimer model^{2,3} a maximum isotope effect should occur when the transition state (TS) is symmetric, which corresponds to a maximum value when ΔG° is close to zero. Bell and Goodall have proposed that this occurs when the pK_a of a carbon acid equals the pK_a of the conjugate acid of the base catalyst.⁴ The pK values of the substrates and bases used, as well as the reaction rate, can be changed over a wide range by mixing solvents. Much work done on the solvent dependence of KIEs has been performed in solvent mixtures as for example dimethyl sulfoxide (DMSO)–water (or alcohols) or acetonitrile–water.^{5–10} Results consistent with an interpretation in terms of the effect of solvent on ΔpK for the reactions have been reported as well as results that indicate that the variation in KIE with solvent cannot be attributed merely to the effect of solvent ΔG° .⁹ One difficulty in interpretation of the latter type of results is that the nature of the solvent species which interacts with the TS is not known for mixed solvents. Some studies of the solvent dependence of KIEs in single solvents have also yielded results that cannot entirely be explained by the variation in ΔG° .^{11–16}

For proton transfer reactions proceeding via carbanion intermediates the importance of a possible internal ion-pair return has to be considered in the interpretation of observed primary KIEs.^{17–21} Scheme 1 shows a simplified internal return mechanism, where the collapse of the ion-pair

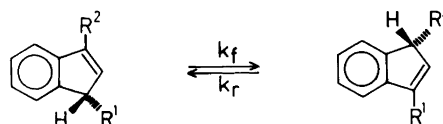
$$k_{\text{obs}} = k_1 k_{-2} / (k_{-2} + k_{-1}) \quad (1)$$



Scheme 1.

back to starting material (k_{-1}) competes with the forward reaction (k_{-2}). Observed rate constants for reactions which proceed according to this scheme are functions of the mechanistic rate constants [eqn. (1)]. This introduces a difficulty in the mechanistic interpretation of observed KIEs, unless the amount of internal ion-pair return is known. The collapse ratio of the ion-pair intermediate is defined as k_{-1}/k_{-2} .

We are interested in the detailed mechanism of stereospecific base-catalyzed 1,3-prototropic rearrangement in the indene system (Scheme 2).^{22–24} This proton transfer is believed to occur via one or, more likely, two hydrogen bonded ion-pair intermediate(s).^{25,26} The consequences of these two possible mechanisms, for the interpretation of KIEs, have been discussed earlier.²⁷



Scheme 2.

Primary deuterium and secondary β -deuterium KIEs have been reported for the rearrangement of 1-methylindene ($R^1 = \text{CH}_3$, $R^2 = \text{H}$) to 3-methylindene.²⁸ These

studies were performed in the solvents toluene and DMSO at 20 °C, using different tertiary amines of varying basicity as catalysts. As an example, a primary deuterium KIE of 5.03 ± 0.06 was reported for this substrate when DABCO was used as a base catalyst in toluene. In DMSO the corresponding KIE is 7.29 ± 0.07 . The primary KIEs reported in that investigation range roughly from 5 to 8, i.e. they are rather large, although the pK difference between the substrate 1-methylindene and the conjugate acids of the amines is larger than 10 for all the amines used, a situation which is far from that where the KIE maximum is expected. Moreover, for a comparable change of reaction rate, the change in KIE is larger when the solvent is changed from toluene to DMSO, than when the base is changed. A difficulty in the interpretation of these results is that the collapse ratio of the postulated ion-pair intermediates is not known. The amount of internal ion-pair return (k_{-1} in Scheme 1) has been estimated to be small.^{29,30} If this is true, the observed KIE will equal the KIE for the rate-determining proton-abstraction step (k_1 in Scheme 1). A significant amount of internal return will however, if k_{-1} is isotopically sensitive, lead to a more complex situation, where the isotope effect of either, or both, k_1 and k_{-1} may change with the solvent.

By using the 'symmetrically' substituted 1,3-dimethylindene as the substrate³¹ (see Scheme 3), the difficulties arising from any possible internal ion-pair return may be eliminated. This substrate has the advantage that the observed KIE is equal to the KIE for the elementary rate-determining proton-abstraction step, assuming fast equilibration of the ion-pair intermediates.²⁷ The collapse ratio is in this case equal to unity. Eqns. (2)–(4) give the relation between phenomenological and mechanistic rate constants. (The phenomenological rate constant $k = k_f = k_r$ in Scheme 2).

$$k = k_1 / \{2 + (k_{-1}/k_{12})\} \quad (2)$$

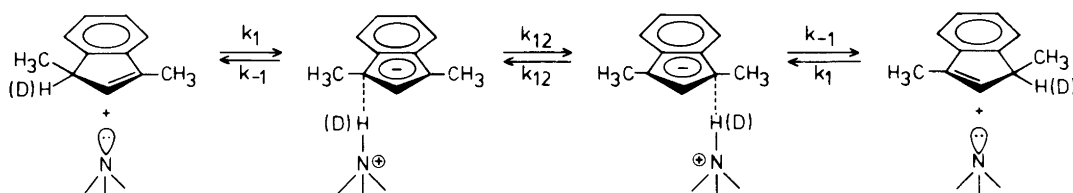
$$k = 1/2 k_1; \text{ if } k_{12} \gg k_{-1} \quad (3)$$

$$k^H/k^D = k_1^H/k_1^D \quad (4)$$

Since 1,3-dimethylindene provides an opportunity to study an elementary reaction step (provided $k_{12} \gg k_{-1}$), this substrate is suitable for different kinds of mechanistic in-

vestigation of proton transfer. It was recently used in a study of the base dependence of the primary KIE, together with the substrate 1-methylindene.²⁷ In that investigation the similarity in the KIE pattern for the two substrates was striking and indicated that the amount of internal ion-pair return for 1-methylindene was negligible. In another investigation, KIEs of 4.0 ± 0.2 , 5.0 ± 0.3 and 4.8 ± 0.3 were obtained for 1,3-dimethylindene in the solvents benzene, pyridine and methanol, respectively, with the use of DABCO as the catalyst at 30 °C.¹⁶ The ΔG^\ddagger values were almost the same in these solvents and can thus not explain the differences in KIE.

With the aim of achieving a deeper knowledge of the solvent dependence of the KIE, we decided to perform a primary deuterium KIE study for the base-catalyzed 1,3-prototropic rearrangement of 1,3-dimethylindene and 1-methylindene in different solvents at 20 °C. The solvents used are toluene, *o*-dichlorobenzene (*o*-DCB) and DMSO. These solvents differ in polarity, having dielectric constants of 2.38, 9.93 and 49, respectively. The choice of solvents is to facilitate comparison with earlier studies of proton transfer in the indene system. Toluene, being a relatively non-polar solvent, probably has little interaction with the activated complex or with the reactant molecules. It has previously been chosen for being well suited for comparison of experimental results with those from model calculations.³² The polar aprotic solvent DMSO has been used in studies of stereospecificity,^{23–25,33,34} stereoselectivity³⁵ and kinetic resolution^{36,37} as well as in a rate-equilibrium³⁸ and a KIE study.²⁸ A TS with considerable charge separation should be better stabilized than the reactant molecules by a solvent of this type. *o*-Dichlorobenzene has, for various reasons, been used in enantioselective rearrangement experiments³⁹ and recently we reported primary deuterium KIEs for the base-catalyzed rearrangement of 1-methylindene and 1,3-dimethylindene in this solvent at 30 °C.²⁷ Its properties put this solvent somewhere in between the other two. Two amines that differ in basicity have been used as base catalysts, namely DABCO and quinuclidine. They are both conformationally rigid and structurally very similar tertiary amines and therefore supposed not to exhibit differences in steric hindrance. High stereospecificity has been obtained even in DMSO, using DABCO as a base catalyst, in earlier investigations of 1,3-proton transfer in the indene system.^{23,24}



Scheme 3.

Results and discussion

The kinetic data have been obtained by the use of a polarimetric differential method.^{28,40} This method has the advantage of permitting both isotopic rate constants and their ratio to be determined simultaneously in one kinetic experiment, thus avoiding interexperimental errors. The experiments start from an isotopic quasi-racemic mixture of the (–)-enantiomer of the protic substrate and the (+)-enantiomer of the deuteriated substrate (or vice versa). The reaction is followed by observation of the optical rotation as a function of time, and from these data the rate constants and their ratio are determined.

The conjugate acids of the bases DABCO and quinuclidine have *pK* values of 8.4 and 9.6, respectively, as determined in the solvent DMSO at 25 °C by Meurling.³⁸ They have both been used in previous studies of base-catalyzed rearrangement in the indene system together with some conformationally rigid aza-adamantanes of varying basicity.^{27,28} In these investigations the amine DABCO shows deviating behaviour, giving the lowest KIE despite its intermediate basicity in comparison with the other structurally similar amine catalysts used. For the other amines the KIE is almost constant. However, as expected from the Melander–Westheimer model, a somewhat higher value is observed for the strongest base.

Table 1. Observed second-order rate constants and primary KIEs for the rearrangement of 1-methylindene^a to 3-methylindene, catalyzed by the base DABCO at 20 °C.

Solvent	[Base] M	$k^H/[B]^{b,c}$ $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	k^H/k^D ^d
Toluene	0.23	0.87(3)	5.03(6) [12] ^e
<i>o</i> -DCB	0.015–0.21	2.01(5)	5.65(8) [2]
Pyridine	0.0295	4.01(8)	6.6(4) ^f
DMSO	0.015	26.4(8)	7.29(7) [3] ^e

^aThe concentration of substrate was 0.09–0.5 M. ^b[B] = base concentration. ^cThe rate constants are statistically corrected for the number of nitrogens. ^dThe number of kinetics runs is given in brackets after each KIE value. ^eTaken from Ref. 28. ^fTaken from Ref. 16.

Table 2. Observed second-order rate constants and primary KIEs for the rearrangement of 1-methylindene^a to 3-methylindene, catalyzed by the base quinuclidine at 20 °C.

Solvent	[Base] M	$k^H/[B]^b$ $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	k^H/k^D ^c
Toluene	0.096	6.9(2)	6.06(6) [2] ^d
<i>o</i> -DCB	0.038	27.5(8)	6.72(8) [3]
DMSO	0.0063	122(8)	7.8(1) [4] ^d

^aThe concentration of substrate was 0.09–0.5 M. ^b[B] = base concentration. ^cThe number of kinetic runs is given in brackets after each KIE value. ^dTaken from Ref. 28.

Table 3. Observed second-order rate constants and primary KIEs for the rearrangement of 1,3-methylindene,^a catalyzed by the base DABCO at 20 °C.

Solvent	[Base] M	$k^H/[B]^{b,c}$ $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	k^H/k^D ^d
Toluene	0.74	0.0200(5)	3.93(6) [3]
<i>o</i> -DCB	1.04	0.051(2)	4.23(7) [3]
Pyridine	1.37	0.108(4)	5.5(3) ^e
DMSO	0.30	0.85(2)	5.91(7) [2]

^aThe concentration of substrate was 0.3 M. ^b[B] = base concentration. ^cThe rate constants are statistically corrected for the number of nitrogens. ^dThe number of kinetic runs is given in brackets after each KIE value. ^eTaken from Ref. 16.

Table 4. Observed second-order rate constants and primary KIEs for the rearrangement of 1,3-methylindene,^a catalyzed by the base quinuclidine at 20 °C.

Solvent	[Base] M	$k^H/[B]^b$ $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	k^H/k^D ^c
Toluene	0.18	0.16(1)	4.73(6) [2]
<i>o</i> -DCB	0.41	0.64(1)	5.21(8) [3]
DMSO	0.24	5.1(1)	6.63(6) [3]

^aThe concentration of substrate was 0.3 M. ^b[B] = base concentration. ^cThe number of kinetic runs is given in brackets after each KIE value.

In Tables 1–4 are listed second-order rate constants (calculated from the pseudo-first-order rate constants by division by the base concentration) and primary KIEs, obtained in kinetic runs in the different solvents. The data in the tables show that, for both bases and in all the solvents used, the rate constants are lower for 1,3-dimethylindene than for 1-methylindene. This is in accordance with the lower acid strength expected for the former substrate. * The value of ΔpK , between the substrate and the conjugate acid of the base-catalyst, is thus larger for 1,3-dimethylindene and the primary KIEs are consistently lower.

For both substrates an increase in the KIE is observed when changing from toluene to the more polar solvents. According to the Hammond postulate an earlier TS is expected in the more polar solvents, in which the charge-separated TS is better stabilized than the non-polar reactant molecules. For an endoergic reaction an earlier TS is more symmetric thus yielding a higher KIE (see Fig. 1).

The observed KIEs increase not only with solvent dielectric constant but also with solvent viscosity. For the degenerate rearrangement of 1,3-dimethylindene (Scheme 3) the charge separation is identical in the postulated ion-pair intermediates and closely similar in the TS

* The difference in *pK_a* between the two substrates can be roughly estimated as 2.4, by comparison with the known *pK_a* values for indene (20.1, DMSO) and 3-methylindene (22.5, DMSO).⁴¹

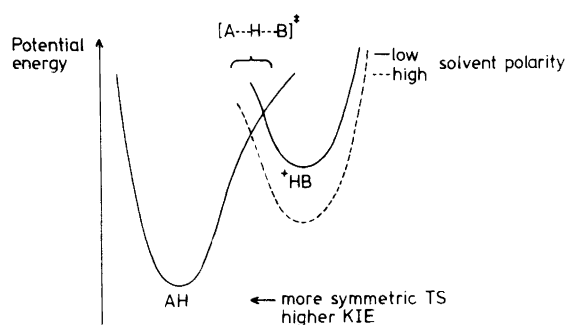


Fig. 1. Qualitative picture of the improved stabilization of a charge-separated TS in a more polar solvent.

for their interconversion. Therefore, the rate constant for ion-pair equilibration, k_{12} , may be expected to be independent of solvent polarity, but might still depend on the viscosity of the solvent. However, the viscosity becomes important in determining the rate only for a process which is at least partly diffusion-controlled, i.e. in this case when $k_{12} \gg k_{-1}$. Thus, a marked variation of k_{12} with solvent appears only under circumstances when the observed rate is independent of k_{12} . For cases where the inequality ($k_{12} \gg k_{-1}$) is not valid the observed rate will depend on the ratio k_{-1}/k_{12} [eqn. (2)]. Here k_{12} is rather insensitive to both viscosity and dielectric constant of the solvent, as discussed above. The rate constant k_{-1} , for the internal return of the ion-pair intermediate, is presumably also insensitive to solvent polarity, since the TS is expected to be structurally similar to the intermediate. Both the intermediate and the TS for its formation have a high degree of charge separation and will thus be better stabilized by a more polar solvent. In conclusion, the observed rate constant k_{obs} will vary as the rate constant k_1 for the proton-abstraction step.

If the assumption regarding fast equilibration of the ion-pair intermediates holds for the rearrangement of 1,3-dimethylindene, the observed KIEs can be identified with the KIEs for the proton-abstraction step. The plausibility of this assumption has been discussed more exhaustively in an earlier paper²⁷ and experiments intended to shed light on this question are in progress and will be reported subsequently. In the following discussion the validity of this assumption is assumed. The KIE values displayed in Tables 3 and 4 thus are assumed to reflect the influence upon solvent change for an elementary reaction step. For the substrate 1-methylindene the situation is more complicated since there is a possible effect from internal return, the amount of which may be different in different solvents. However, there is a similar trend both in the rate constants and the KIEs obtained for this substrate (Tables 1 and 2) compared with 1,3-dimethylindene. This suggests that the observed solvent dependence of the KIE can be interpreted in terms of effects on the proton abstraction step.

Caldin and Mateo⁴² reported a strong solvent dependence of the KIE for the reaction of 4-nitrophenylnitro-

methane with tetramethylguanidine in aprotic solvents. Their observations of k^H/k^D values between 11 and 50 at 25°C were interpreted in terms of tunneling. The unusually large KIEs of 40–50 were found in non-polar solvents such as toluene, while in more polar solvents such as acetonitrile, the KIEs were much smaller (10–13). They suggested that motions of solvent molecules are coupled with the motion of the hydron in the more polar solvents, resulting in an increase in the effective mass of the hydron in flight and a decrease in the amount of tunneling. A large tunneling effect could be expected in less polar solvents, where the hydron is the only atom with appreciable movement in the TS of the rate-determining step. However, the interpretation of the high KIE values in terms of tunneling has been questioned by Rogne *et al.*^{43–46} who reported that the reaction was complicated by isotopic exchange from the deuterated substrate. Taking such exchange into account lowered the large KIEs to values around 11, i.e. within the limits of semi-classical theory. Recently, Kresge and Powell⁴⁷ reported rates of loss of tritium from 4-nitrophenylnitromethane- α -*t* catalyzed by a series of amine bases. They concluded that the large KIEs reported by Caldin and Mateo were determined under conditions where the isotopic label was lost and are therefore artefacts. Using the relationship proposed by Swain *et al.*⁴⁸ they obtained a value of around 12 for k^H/k^D for the reaction of the substrate with tetramethylguanidine in toluene.

Another proposal for the treatment of the solvent dependence of the KIE within the tunneling model has been made by Sugimoto *et al.*¹¹ They reported, for the reaction of trinitrotoluene with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), KIEs of 19.1 in acetonitrile and 29.9 in the less polar 1,2-dichloroethane at 25°C. In their calculations of the tunneling correction factors they assumed that there is no change in effective mass of the hydron in transfer. The tunneling corrections they obtained showed a clear solvent dependence, which they explained in terms of the relative magnitude of the barrier height. Increasing solvent polarity decreases the barrier height and thus reduces the amount of tunneling.

Another observation of higher KIE values in toluene compared with the more polar solvent acetonitrile has been reported for the reaction between 1-(4-nitrophenyl)-1-nitroethane and DBU at 25°C.¹³ The KIEs obtained, 12.0 and 7.8 in toluene and acetonitrile, respectively, are not as high as those given for the example above but the pattern in the solvent dependence of the KIEs is the same in both these investigations.

Our observations of an increase in KIE when changing to more polar solvents are contradictory to the predictions based on the tunneling model. Since the KIEs we report are all smaller than 8 this indicates that there is presumably no significant contribution from tunneling in the reactions studied. However, a value of the KIE in this range does not necessarily exclude tunneling. A more reliable criterion of tunneling is the appearance of a curved Arrhenius plot obtained from a study of the temperature dependence.⁴⁹

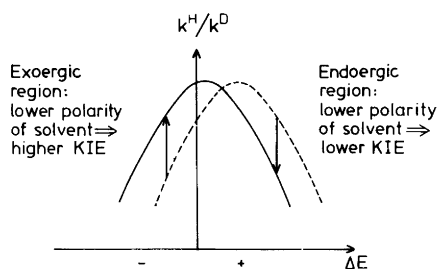


Fig. 2. Qualitative picture of the influence of solvent polarity on the free energy dependence of k^H/k^D . The solid and dotted lines represent low and high solvent polarity, respectively.

The quantum-statistical mechanical model (QSM)^{50–52} offers an alternative to the TS-theory based formulation of kinetic isotope effects. Sühnel has applied the QSM, in the version of Dogonadze and coworkers,⁵² to the study of proton-transfer reactions where the influence of factors such as steric hindrance⁵³ and solvent polarity⁵⁴ on KIEs has been explicitly taken into account. According to the treatment by Sühnel and Gustav,⁵⁴ the solvent dependence of the KIE originates mainly from three sources: reaction free energy (ΔE), solvent reorganization energy (E_s) and intermolecular interaction potential [$U(R)$]. The reaction free energy decreases with increased solvent polarity for reactions in which two neutral molecules are transformed into an ion-pair. For an endoergic reaction, as in the present case, this factor results in an increased KIE as has already been discussed above. The value of E_s affects the curvature of the free energy plot for the KIE. The larger the E_s , the broader the curves.⁵¹ In passing to more polar solvents an increase in reorganization energy is expected and this leads, except for a small range around $\Delta E = 0$, to an increase of the KIE. The third contribution, the intermolecular interaction potential $U(R)$, appears to be the dominant one. $U_i(R)$ (i = initial state) is only slightly dependent on the solvent, whereas the difference $U_f(R) - U_i(R) < 0$ (f = final state), is expected to be more negative with increasing solvent polarity. The consequences of this for the dependence of KIE on solvent polarity are illustrated in Fig. 2. For exoergic reactions a decrease in the KIE is expected in passing to more polar solvents, whereas endoergic reactions show a corresponding increase in KIE.

The results referred to above^{11,13} are in agreement with the QSM prediction for exoergic reactions. The variation of the KIE with solvent is quite large in at least one of these cases, and it was concluded by Sühnel and Gustav⁵⁴ that differences in intermolecular interaction potential must be invoked in order to explain this. For the endoergic region no experimental data were available. The present investigation, however, constitutes such an example. For endoergic reactions the contributions from ΔE , E_s and $U(R)$ all tend to increase the KIE with increasing solvent polarity. This is in accordance with the present results. Since the present variations of the KIE with solvent are rather small, it is difficult to single out any one of the three factors as being more important than the others.

Experimental

Optical rotation was measured with a Perkin–Elmer 241 photoelectric polarimeter. The kinetic runs were performed with the same instrument, equipped with an automatic data-acquisition system consisting of an ABC 80 with a floppy disc unit FD 4U. The water-jacketed polarimetric cell (optical path length 10 cm, volume 0.9 cm³) was connected to a HETO 02 PT 623 proportional regulating thermostat. The temperature was measured with a calibrated mercury thermometer, with an absolute accuracy of 0.02 °C, at the outlet of the cell. The temperature did not deviate more than 0.03 °C from the average value during the runs and was thus 20.00 ± 0.05 °C.

The synthesis and purification of the optically active and isotopically substituted substrates 1-methylindene³⁸ and 1,3-dimethylindene^{27,31} have been described earlier. The rotation of each batch of purified indene was measured in a short polarimetric microcell (optical path length 1 cm, vol-

Table 5. Optical rotations of (*R*)-(–)-1-methylindene and (*R*)-(+)-1-methyl(1,3-²H₂)indene. The specific rotations were measured in *o*-dichlorobenzene solution.^{a,b}

λ/nm	$0.1\alpha^{20.0}$ (neat)	$[\alpha]^{20.0}$
578	–20.24	–204.2
	+20.76	+209.2
546	–23.37	–235.6
	+23.97	+241.7
436	–43.59	–438.8
	+44.78	+451.0
365	–78.94	–794.8
	+81.23	+818.4

^aThe accuracy is ± 0.5 %. ^bSpecific rotations in toluene and DMSO are reported in Ref. 28.

Table 6. Optical rotations of (*R*)-(–)-1,3-dimethylindene and (*S*)-(+)-1,3-dimethyl(1-²H)indene.^a

λ/nm	$0.1\alpha^{20.0}$ (neat)	Toluene	$[\alpha]^{20.0}$ <i>o</i> -DCB	DMSO
578	–15.64	–168.1	–166.7	–167.2
	+16.11	+173.6	+170.7	+173.5
546	–18.08	–196.4	–192.6	–193.2
	+18.63	+199.7	+197.3	+199.5
436	–33.90	–368.7	–361.8	–363.8
	+35.01	+375.1	+370.8	+374.7
365	–61.94	–669.4	–660.3	–664.0
	+64.15	+690.4	+678.7	+690.5

^aThe accuracy is ± 0.5 %.

ume 0.09 cm³, neat). Optical rotations measured neat and in the different solvents are collected in Tables 5 and 6.

The preparation and purification of the amines quinuclidine and DABCO along with the purification of the solvents have been described earlier.^{27,28} All handling of the purified amines was carried out in a glove box, in which the atmosphere was circulated through molecular sieves (5 Å) in the presence of Ascarite to lower the amount of carbon dioxide in the atmosphere. The glove box was flushed with nitrogen before use. The flasks containing the stock solutions of the amines were stored in larger bottles filled with dry nitrogen and containing silica gel together with KOH pellets.

Acknowledgements. Valuable comments by Dr. J. Sühnel are much appreciated. We also thank Professor G. Bergson for discussions. This project is financially supported by the Swedish Natural Science Research Council.

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Received March 12, 1990.