Complexes of 1,2-Dipiperidinoethane with an Isoprenyllithium Oligomer

Stanley Bywater,* Paul Black, and Denis J. Worsfold

Division of Chemistry, National Research Council of Canada, Ottawa K1A 0R9, Canada

François Schué

Université des Sciences et Techniques du Languedoc, 34060 Montpellier, France.

Received June 27, 1984

ABSTRACT: The formation of complexes between lithium and chelating diamines is important in microstructure modification during anionic diene polymerization. A ^{13}C and ^{1}H NMR study has been made of the complexes formed by 1,2-dipiperidinoethane with the one-unit model chain prepared by addition of *tert*-butyllithium to isoprene. Evidence is presented for the formation of three different complexes. Two of them, a monosolvated dimeric lithium compound and a similarly solvated monomeric lithium compound, have previously been reported for complexes with tetramethylethylenediamine. The latter, however, is less easily formed with dipiperidinoethane and has a trans structure rather than the more usual cis one. A third complex, a monosolvated lithium tetramer, can be detected at low dipiperidinoethane/lithium ratios.

Introduction

The use of complexing agents to influence the microstructure of polydienes prepared anionically is a well-established phenomenon.[1] In particular the use of chelating polyamines in concentrations roughly equivalent to lithium concentration allows the production in hydrocarbon solvents of polydienes with high vinyl contents. Tetramethylethylenediamine (TMEDA) has been frequently used in this manner,[2] but more recently the use of 1,2-dipiperidinoethane (DIPIP) has been found to produce polybutadiene of higher 1,2 content than other systems.[3] A systematic investigation on DIPIP-containing systems has therefore been initiated in an attempt to elucidate the reasons for its particular effectiveness. Preliminary results on both butadiene and isoprene polymerization have been presented.[4] This paper examines the behavior of an isoprene model system, the one-unit model prepared from *tert*-butyllithium and isoprene. Similar examinations of the nature of the complexes formed in the case of TMEDA have been previously made by spectroscopic and other methods.[5-8] A parallel study of DIPIP-containing systems is therefore of value.

Experimental Section

The preparation of the 1:1 adduct of *tert*-butyllithium and isoprene has been adequately described earlier.[9] In order to remove the small amounts of two-unit material always present, it was converted to the corresponding mercury compound, distilled under reduced pressure, and reconverted to the lithium compound by treatment with lithium suspension.[10] The solvent used was cyclopentane purified in the manner described previously for all hydrocarbon solvents.[4] 1,2-Dipiperidinoethane (Aldrich) was distilled under reduced pressure, transferred to the vacuum line, and subsequently distilled off CaH_2 into breakseals as required. All manipulations were carried out in vacuo. The DIPIP concentration was estimated gas chromatographically on the H_2O-terminated solutions after NMR study. ^{1}H and ^{13}C NMR studies were carried out on ~0.5 M solutions in a Varian XL-100 instrument, coupled to a Nicolet Fourier transform system. Chemical shifts are quoted on the δ scale (ppm from Me_4Si). ^{1}H measurements were made in the CW mode, the solvent cyclopentane ($\delta_{Me_4Si} = 1.508$) being used as secondary reference. ^{13}C measurements were made in the FT mode; pulse width 5 μs (flip angle ~20°); acquisition time, 0.82 s; pulse delay 0.5 s. The solvent was again used as secondary reference ($\delta_{Me_4Si} = 26.50$).

Results

One of the major characteristics of the ^{1}H NMR spectrum in hydrocarbon solvents of $RCH_2CHC(CH_3)CH_2Li$, where R = *tert*-butyl or other alkyl groups, is the presence of two triplets attributed to the proton on the γ carbon in cis and trans forms.[10] These are resolved in benzene (~66% trans at lower field) but overlapped in cyclopentane. The signals from this proton (and the corresponding carbon) are particularly sensitive in position to the lithium environment. They occur in a region of the spectrum clear of other signals and so are easily identified under all conditions. Signals from the α position are similarly sensitive but are often in a crowded region and more difficult to identify. The rest are relatively insensitive to environment. As DIPIP/lithium ratio (R) is increased at room temperature the triplets separate, move upfield to increasing extents, and change in relative intensity. The behavior is similar to that observed on the addition of other polar molecules such as tetrahydrofuran, differing only in that much less material is required for pronounced effects. Below $R \sim 0.2$ the higher field triplet appears to have another signal superposed but by $R = 0.3$ simplification to a well-resolved triplet has occurred, which moves upfield until R reaches a value of around 0.6–0.7 and then essentially is insensitive in position to further DIPIP additions. The initially lower field triplet (attributable to trans structures) on the other hand moves progressively upfield at all DIPIP ratios studied, moving past the other triplet at an R value ~0.8. Its intensity decreases up to this point but increases again as it moves to higher field. The results are illustrated in Figure 1; chemical shifts and trans structure percentage are given in Figure 2.

Similar results are obtained from ^{13}C NMR studies at room temperature as shown in Figure 3. The γ-carbon signal, initially broad if R is less than ~0.4, sharpens gradually at higher R, and in addition an extra signal begins to appear from $R \approx 0.6$, gradually increasing in intensity as it moves upfield. The major signal stabilizes in position in the region of $R = 0.5$–1.0 but the minor signal does not. As with the ^{1}H NMR studies these are obviously signals averaged over more than one species, probably different aggregates, cis/trans isomerization being slow on the NMR time scale, so that separate cis and trans averaged signals are observed. Interesting results are, however, observed at lower temperature when exchange averaging is slowed down. At −20 °C for example, at $R < 0.6$ the γ signal separates into still broad signals (a) in the region 102–104 ppm (typical of uncomplexed material), (b) ~97 ppm, and (c) ~90 ppm (Figure 4). As R is increased, (a) decreases and (b) goes through a maximum at $R \sim 0.25$ until at $R = 0.5$ and upward, species (c) is the major constituent. At $R > 0.6$, however, a further weak signal (d)

0024-9297/85/2218-0335$01.50/0

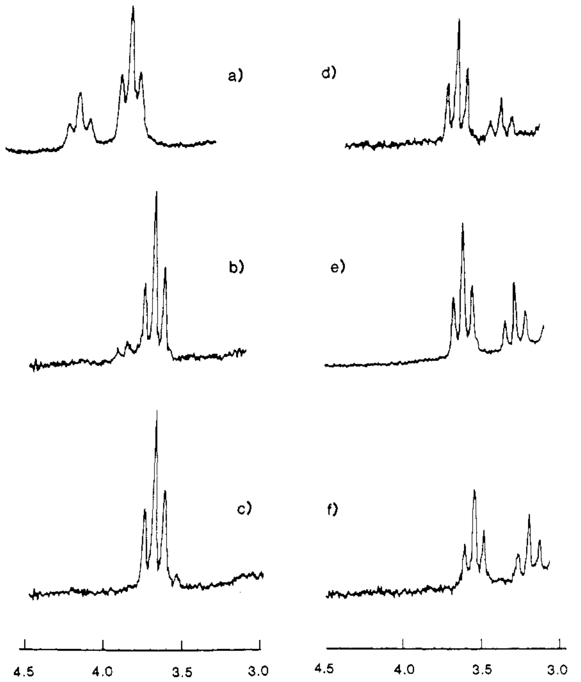

Figure 1. ^{1}H NMR spectra of the γ-CH proton at room temperature: (a) $R = 0.37$; (b) $R = 0.62$; (c) $R = 0.88$; (d) $R = 2.25$; (e) $R = 3.65$; (f) $R = 4.25$.

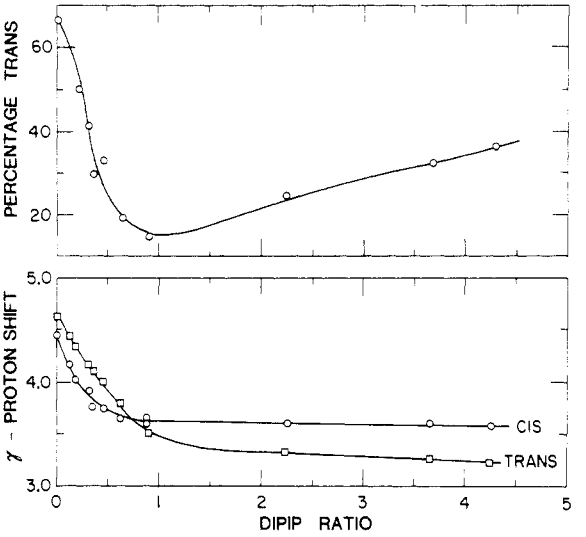

Figure 2. Percentage of trans structures (upper) and chemical shifts of cis and trans γ protons (lower) as a function of R. The assignments are confirmed by ^{13}C NMR.

is visible at higher field (69.8 ppm), which increases in intensity as R is increased. The two signals (c) and (d) are the only ones detectable at high R. As noted above, (c) at higher temperature stabilizes in position, essentially at the -20 °C position for $R > 0.6$. The results, together with the data in Figure 2, imply that it corresponds to a single aggregate whose molecules are cis in configuration. The weaker signal (d) is variable in shift at room temperature, corresponding to a signal averaged over trans structures. One should, therefore, see at -20 °C its partner, which is probably (b). From the position of the averaged shifts and taking into account the relatively low proportion of trans structures present, (b) would not be detectable above $R = 0.6$ (i.e., <5%).

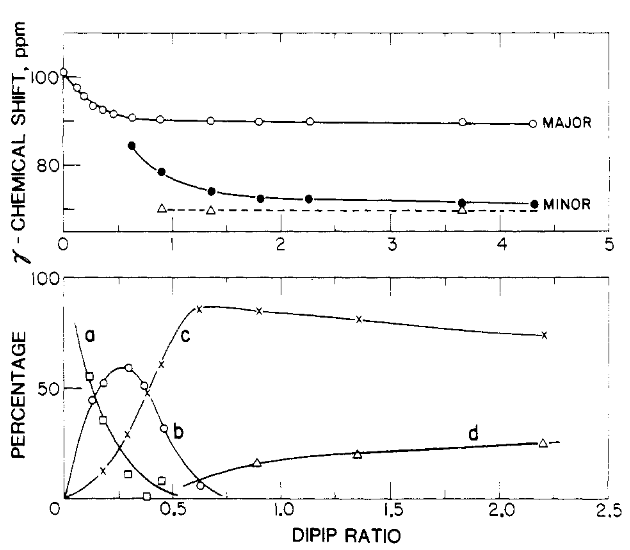

Figure 3. (Upper) ^{13}C chemical shifts of the γ carbon at ~25 °C. (△) Chemical shift of the minor component at -20 °C. (Lower) Percentage of signals (a), (b), (c), and (d) as defined in the text at -20 °C.

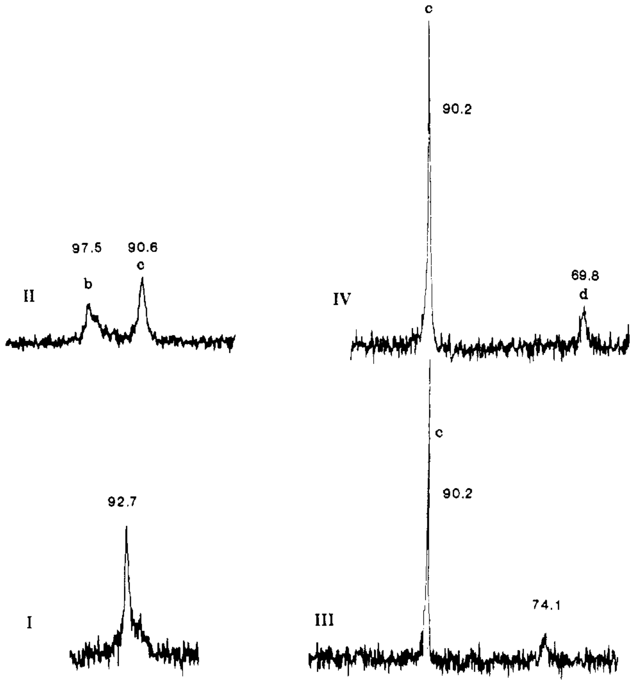

Figure 4. Examples of ^{13}C γ-carbon signals and their temperature variation. (I) $R = 0.37$, ~25 °C, broad overlapped signals, probably cis and trans. (II) $R = 0.37$, -20 °C, broad signals (b) and (c). A very small (a) signal is observed in other preparations with roughly the same R. (III) $R = 1.35$, ~25 °C, sharper signals typical of $R > 0.6$. (IV) $R = 1.35$, -20 °C, signals (c) and (d).

Integration of the areas of the four components at -20 °C as a function of R produces the curves shown in Figure 3. Species (a) is clearly the original unsolvated tetramer. Species (b) is already the major component in solution at $R = 0.25$–0.3 and hence the only plausible structural assignment is a singly DIPIP-solvated tetramer. A solvated trimer is an unlikely candidate given the structure of the unsolvated material. By $R = 0.5$ species (c) is the major component and remains so at all higher R values. It must be either a dimer solvated with one molecule of DIPIP or the tetramer solvated with two. The former is more likely. The high cis content of the solutions confirms that this is essentially in the cis form. Species (d), which only slowly builds up on further DIPIP addition, forms less readily, requiring a large excess of added DIPIP to form even ~30% of the total material. From the stoichiometry, no evidence of its aggregation state can be obtained but a monomeric monosolvated lithium compound seems likely. Its configuration must be trans from the arguments above and because the trans content increases in parallel with its appearance.

Up to $R \sim 0.5$ in fact, the proportions of the four different species given in Figure 3 account for all the DIPIP added; i.e., addition of the DIPIP/lithium ratios required for the fraction of unsolvated tetramer, monosolvated tetramer, and solvated dimer equals within experimental error the added DIPIP/lithium ratio. At $R \sim 0.6$ and higher, it is clear that free DIPIP must be present since the proportion of DIPIP required is less than that added. Confirmation that this is so can be obtained from the ^{13}C signals from DIPIP itself. Only one set is observed, indicating that it is equilibrating rapidly among all species present. Normally the carbons adjacent to nitrogen in the free compound in cyclopentane solution resonate at 58.03 (linking) and 55.80 ppm (ring). At R values less than 0.5, only a single signal is observed in our instrument at 56.50 ppm. Presumably conformational changes associated with the complexing process have equalized (or nearly so) these shifts. Already at $R = 0.6$, the signals are separated by 0.25 ppm, the separation increasing gradually with R but never attaining the $\Delta\delta$ value of 2.23 ppm even at $R \sim 4$. It is clear that the first-formed solvates have $\Delta\delta \sim 0$ ppm, and although it may not be true for higher solvates, it seems reasonable to suppose that their $\Delta\delta$ is not large and that the main source of the signal separation is the presence of free DIPIP. A simple calculation based on a two-site model indicates that ~70% of the lithium is complexed at the higher ratios used. Since only 50% would be required for dimer formation (species (c)) it follows that species (d) is likely to be an unassociated lithium compound complexed with DIPIP.

Discussion

It is of interest to compare these results with those previously reported on interaction of the same lithium compound with TMEDA and PMDT (pentamethyldiethylenetriamine).[5–7] At present, only ^{1}H NMR data are available at room temperature but comparisons are possible. The cis content with TMEDA reaches essentially 100% at $R \sim 0.5$; i.e., only a cis γ triplet is observable. This continues to move upfield until slightly above $R = 1$, indicating that more than one cis species is in equilibrium. The presence of a monosolvated cis dimer and a monosolvated cis monomer were suggested, the latter of course increasing in proportion as R increases. With PMDT, the same conversion to cis was observed by $R = 0.5$ but the cis triplet's position did not drift upfield as more PMDT was added. This was taken to mean that dissociation to the monomer did not occur to any significant extent. The behavior of DIPIP is somewhat different, although it is clear that the cis dimer is again easily formed. A monomer can be formed apparently as with TMEDA but not to such an extent, and the structure must be trans rather than cis. The formation of trans allylic lithium compounds in fact seems a characteristic of DIPIP, since the majority of solvating agents convert dienyl anion pairs primarily to monomeric cis species.[10,11] The monomeric trans form is more readily formed with butadienyllithium. ^{13}C NMR experiments of the same type made on the corresponding *tert*-butyllithium addition product showed that the amount of trans material *increased* continuously with R, reaching 93% at $R = 2$ and virtually 100% at $R = 5$.[4] The averaged trans γ signal was still changing at $R = 2$. This must mean that two trans-containing species exist at high R where only solvated dimer and monomer should be present.[12] Thus in butadiene compounds, the dimers must be at least partly in the trans configuration. In the absence of suitable low-temperature studies, the exact proportion is not clear.

The occurrence of three dipiperidinoethane-solvated entities indicated in the proportions given in Figure 3 only refers, of course, to the particular model used at the given concentrations and temperatures. A 45 °C change in temperature (−20 to +25 °C) does not seem to produce major changes in the proportions, but dilution 500 times to a concentration suitable for actual polymerization would inevitably change the proportions at a given ratio of complexing agent to lithium, at least until only the solvated dimer and monomer were present.[12] The present study is therefore to be regarded only as an indication of the types of solvation which can in principle occur. Two of them have been described previously;[6,7] the present study simply confirms that they indeed can occur with DIPIP as with TMEDA. The solvated tetramer has not previously been suggested, although solvation without dissociation has been suggested for some other lithium compounds.

Registry No. Isoprene, 78-79-5.

References and Notes

(1) T. A. Antkowiak, A. E. Oberster, A. F. Halasa, and D. P. Tate, *J. Polym. Sci., Part A-1* **10**, 1319 (1972).
(2) A. W. Langer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 7 (1), 132 (1966).
(3) A. F. Halasa, D. N. Schulz, D. P. Tate, and V. D. Mochel, *Adv. Organomet. Chem.*, **18**, 55 (1980); A. F. Halasa, D. F. Lohr, and J. E. Hall, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1357 (1981).
(4) D. J. Worsfold, S. Bywater, F. Schué, J. Sledz, and V. Marti-Collet, *Makromol. Chem., Rapid Commun.*, **3**, 239 (1982).
(5) S. Dumas, V. Marti, J. Sledz, and F. Schué, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 81 (1978).
(6) S. Dumas, J. Sledz, and F. Schué, *ACS Symp. Ser.*, **No. 166**, 463 (1981).
(7) V. Collet-Marti, S. Dumas, J. Sledz, and F. Schué, *Macromolecules*, **15**, 251 (1982).
(8) S. Dumas, J. Sledz, F. Schué, S. Raynal, S. Bywater, and D. J. Worsfold, *Polymer*, **24**, 1291 (1983).
(9) F. Schué, D. J. Worsfold, and S. Bywater, *Macromolecules*, **3**, 509 (1970).
(10) S. Bywater and D. J. Worsfold, *J. Organomet. Chem.*, **159**, 229 (1978).
(11) S. Bywater, *ACS Symp. Ser.*, **No. 166**, 71 (1981).
(12) S. Bywater, D. H. MacKerron, D. J. Worsfold, and F. Schué, *J. Polym. Sci., Polym. Chem. Ed.*, in press.