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On the thermodynamic consequences of the threefold isomerism in the LiCN system [α]

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Abstract

The LiCN system which was recently characterized computationally, is considered to be an equilibrium mixture of three isomeric species (lithium isocyanide, a bridged species and lithium cyanide). While the isocyanide prevails at low temperatures, at moderate and higher temperatures the isocyanide and bridged species can exhibit comparable stability or even stability interchange. The overall standard heat capacity at constant pressure shows a clear temperature maximum; the isomeric enhancement of heat capacity can be as high as 19.5 J K^{-1} mol^{-1}. The role of structural fluxionality is discussed briefly.

INTRODUCTION

The triatomic LiCN system has been the subject of constant theoretical interest [1–14] because of both its simplicity and its interesting fluxional behaviour. The computations have added considerably to the observed information [15–17]. According to recent computations [13,14] there are three significant isomeric structures representing the whole LiCN system; however, their interplay was evaluated, at most, in terms of the simple Boltzmann factors [14]. In view of the recent surprising findings [18–20] on strong temperature effects, even within quite simple isomeric systems, this study is devoted to the state-of-art treatment of the LiCN isomeric system, which is, incidentally, related to some extent to the silver fulminate/cyanate system, frequently quoted [18] as the first isomeric system described.

[α] Dedicated to Professor Richard Stephen Berry on the occasion of his 60th birthday.

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THE LiCN ISOMERIC SYSTEM

The LiCN potential hypersurface exhibits [13,14] three significant stationary points: in accordance with ref. 14, referred to as LiNC (lithium isocyanide), LiCN(T) (bridged, T-shaped structure) and LiCN (lithium cyanide). In terms of potential energy [14], the lowest lying is the LiNC species followed by the LiCN(T) and LiCN isomers. So far the most advanced treatment [14] of the LiCN system has been based on the coupled-cluster method [21] using first-order correlation orbitals [22–25]. Table 1 presents the relative potential energy terms (ΔE_i) evaluated [14] in the CCSD + T(CCSD) approach employing the 18s/12p/6d/2f basis set.

The optimum geometry of the LiNC and LiCN species was found [14] to be quasi-linear, i.e. almost but not exactly linear. However, this deviation from linearity may be just a computational artifact. Therefore two approaches to the LiNC and LiCN structures are employed here: either the original quasi-linear structures [14] (C_s symmetry point group) or an idealized linear geometry derived from the quasi-linear one by putting the bond angle equal to π ($C_{\infty v}$ symmetry point group). The alternative approaches to the geometry have substantial consequences at the vibrational-mode level. The original quasi-linear structures possess three vibrational modes each; however, the corresponding strictly linear structures exhibit four normal vibrational modes. The bond-angle deformation mode (conventionally coded as ν_2) becomes twice degenerate upon the non-linear/linear transition. For our $C_{\infty v}$ approach we employed exactly the same harmonic vibrational frequencies [14]; however, the degeneracy factor of the ν_2 mode was changed from 1 to 2.

Using vibrational frequencies [14], the harmonic vibrational contributions to zero-point energy can be evaluated, and thus we can proceed from the relative potential energy terms, ΔE_i, to the relative ground state energy terms, $\Delta H_{0,i}^{\ominus}$, i.e. the standard enthalpy changes at absolute zero temperature (see Table 1). Clearly the third structure, LiCN(T), keeps its C_s symmetry in both treatments of the LiNC and LiCN structures.

TABLE 1

Survey of the relative energetics [14] within the LiCN isomeric system

Species	Non-linear C_s, LiNC and LiCN		Linear $C_{\infty v}$, LiNC and LiCN	
	ΔE_i [a]	$\Delta H_{0,i}^{\ominus}$ [b]	ΔE_i [a]	$\Delta H_{0,i}^{\ominus}$ [b]
LiNC	0.0	0.0	0.0	0.0
LiCN(T)	3.05	3.16	3.05	2.74
LiCN	9.67	9.78	9.67	10.32

[a] Potential energy change (kJ mol^{-1}).

[b] Ground state energy change, i.e. the enthalpy change (kJ mol^{-1}) at absolute zero.

THE CONSISTENT RELATIVE STABILITY REASONING

A straightforward application of the ΔE_i or $\Delta H_{0,i}^{\ominus}$ terms alone for isomeric stability assessments is actually of rather limited use (in fact, the two energy scales need not even yield the same stability order). A first approximation to temperature-dependent isomeric mole fractions in the equilibrium mixture is offered by the simple Boltzmann, configurational or steric factors [26–29]:

$$w_i' = \frac{\exp[-\Delta E_i/(RT)]}{\sum_{j=1}^{n} \exp[-\Delta E_j/(RT)]} \tag{1}$$

where n is the number of isomers, R is the gas constant and T is the temperature. However, the simple w_i' factors cannot cross one another in their temperature courses.

A still higher approximation to the equilibrium isomeric mole fractions, free of the above-mentioned drawback, requires an inclusion [30–32] of the rotational–vibrational motions through the isomeric partition functions, q_i:

$$w_i = \frac{q_i \exp[-\Delta H_{0,i}^{\ominus}/(RT)]}{\sum_{j=1}^{n} q_j \exp[-\Delta H_{0,j}^{\ominus}/(RT)]} \tag{2}$$

In principle, the partition functions q_i could be of any quality; however, with respect to the computationally accessible information they are used here in the usual rigid-rotor and harmonic-oscillator (RRHO) form.

From the point of view of the equilibrium isomeric mixture, it is convenient to consider two limiting situations with the standard thermodynamic terms, $X^{\ominus}$, (or other quantities as well, including spectra): the standard partial terms, $\Delta X_i^{\ominus}$, for (hypothetical) isolated individual isomeric species; or the overall terms, $\Delta X_T^{\ominus}$, belonging to the equilibrium isomeric mixture. Moreover, it is convenient to consider a third type of quantity, namely the isomerism contributions to the thermodynamic terms $\delta_n X_1$ (related to the structure labelled 1 as reference species):

$$\delta_n X_1 = \Delta X_T^{\ominus} - \Delta X_1^{\ominus} \tag{3}$$

The isomerism contributions are free of the common terms and therefore they represent a useful tool for the evaluation of isomeric interplay effects. It has become customary that the species most stable in the low temperature region is chosen as the reference structure, labelled 1. Three quantities X are considered here: enthalpy, $X = H$, entropy, $X = S$, and heat capacity at constant pressure, $X = C_p$. For the last term, two quantities can in fact be considered [33], namely the isofractional contribution, $\delta_n C_{p,w,1}$, referring to the situation with temperature-independent terms, w_i, and the full (relaxa-

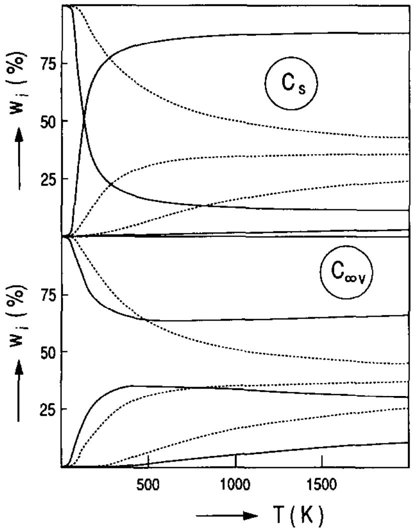

Fig. 1. Temperature dependences of the weight factors w_i (solid lines) and simple Boltzmann factors w_i' (broken lines) of the LiCN isomers in their equilibrium isomeric mixture for both approaches to symmetry of the quasi-linear species LiNC and LiCN (non-linear C_s, linear $C_{\infty v}$). The stability order of the isomers in the low temperature region reads LiNC (most stable), LiCN(T) and LiCN (see Table 1).

tion[a]) contribution i.e. considering that w_i changes with temperature accordingly. Finally, the number of members in the isomeric set, n, can be varied, in each step removing the least stable species; thus the converging properties of the $\delta_n X_1$ terms can be studied.

RESULTS AND DISCUSSION

Figure 1 presents the course of the w_i and w_i' terms evaluated for the two (C_s or $C_{\infty v}$) approaches to the quasi-linear species geometry. There is an apparent difference between the two treatments. In the former situation there is a crossing point of two w_i curves. In the other treatment, however, the two curves exhibit a point of closest approach. The third species (LiCN) is rather insignificant in both cases. Table 2 gives an exact position of the crossing (i.e. equimolarity) or highest coexistence points. While the crossing is practically insensitive to removal of the least stable isomer (LiCN), the highest coexistence position is quite sensitive to isomeric set reduction. In any case, it can be concluded that at moderate and/or higher temperatures

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[a] It should be mentioned that the relaxation heat-capacity isomerism contribution can either denote the full term (eqn. (3)) or only that part of it which remains after subtracting the isofractional component (see refs. 33 and 34).

TABLE 2

Specification of some characteristics [a] in temperature isomeric interplay in the LiCN system

System [b]	Type of point	T (K)	w_1 [c] (%)	$\delta_n C_{p,1}$ (J K^{-1} mol^{-1})
3, C_s	Equimolarity	138	50.0	10.291
2, C_s	Equimolarity	138	50.0	10.277
3, C_s	$\delta_3 C_{p,1}$ maximum	87.5	80.1	19.461
2, C_s	$\delta_2 C_{p,1}$ maximum	87.5	80.1	19.460
3, $C_{\infty v}$	Coexistence	945	61.8	−0.6887
2, $C_{\infty v}$	Coexistence	619	63.8	−1.4089
3, $C_{\infty v}$	$\delta_3 C_{p,1}$ maximum	88.8	93.3	4.9538
2, $C_{\infty v}$	$\delta_2 C_{p,1}$ maximum	88.8	93.3	4.9531

[a] Either a point of equimolarity of two species, a point of the closest mutual approach ("coexistence") or the maximum in the isomerism contribution to heat capacity, $\delta_n C_{p,1}$.

[b] Number of isomers considered (2 or 3, with LiCN being excluded or included), and the symmetry of the quasi-linear species LiNC and LiCN (non-linear C_s, linear $C_{\infty v}$).

[c] The mole fraction of the LiNC structure in the isomeric equilibrium mixture.

the LiNC and LiCN(T) species should be present in comparable amounts in the equilibrium mixture, while the LiCN species remains present in a smaller amount. The ground state energy structure, i.e. the supposed global energy minimum, LiNC, need not necessarily be the relatively most stable species throughout. Finally, the simple Boltzmann factors have reasonable values only at some temperatures.

Figure 2 shows the temperature course of the isomerism contributions, $\delta_n X_1$, to the thermodynamics of the LiCN system (the isomerism contribution to the system enthalpy, $\delta_n H_1$, entropy, $\delta_n S_1$, and heat capacity, $\delta_n C_{p,1}$, as well as its isofractional portion, $\delta_n C_{p,w,1}$, related to the LiNC isomer as reference structure). The isomerism contributions are clearly significant for a precise evaluation of the overall thermodynamic terms even at quite low temperatures. The isomerism contribution to heat capacity exhibits a typical [33] temperature dependency with a clear maximum (its positions are specified in Table 2). While in the C_s approach the differences caused by removing the LiCN species from the isomeric set are rather insignificant, this is not the case in the $C_{\infty v}$ approach at higher temperatures (which is, of course, in accord with the findings of Fig. 1). However, the position of the heat capacity maximum is, in both approaches, insensitive to a consideration of the third isomer.

The isomerism contributions to thermodynamics, although useful, represent only an auxiliary technical term as they cannot be observed directly. Therefore Fig. 3 presents the standard heat capacity at constant pressure, $C_p^{\ominus}$, evaluated for the single LiNC isomer and for the three-membered isomeric mixture. The plots demonstrate that the LiCN isomerism should be manifested in an observable temperature maximum of the standard $C_p^{\ominus}$ term.

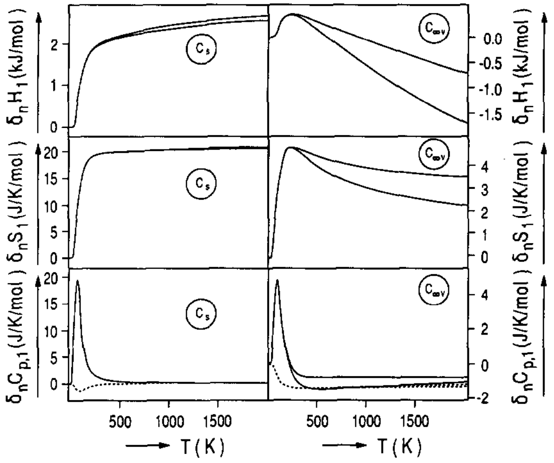

Fig. 2. Temperature dependences of the isomerism contributions, $\delta_n X_1$, to enthalpy ($X = H$), entropy ($X = S$) and heat capacity ($X = C_p$) related to the LiNC isomer as the reference species for both approaches to symmetry of the quasi-linear species LiNC and LiCN (non-linear C_s, linear $C_{\infty v}$). The higher and lower curve in each pair corresponds to the three- and two-membered isomeric set respectively. For heat capacity, the isofractional $\delta_n C_{p,w,1}$ components are given (broken lines) in addition to the full (relaxation) term.

There are rather substantial quantitative differences between the results from the C_s and $C_{\infty v}$ approaches, caused primarily by the fairly low value of the bond-angle deformation mode for the quasi-linear species. Alternatively,

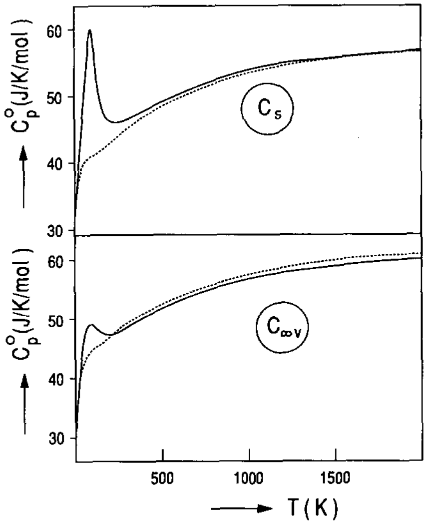

Fig. 3. Temperature dependences of the standard heat capacity at constant pressure, $C_p^{\ominus}$, for the equilibrium LiCN isomeric mixture (solid line) and for the sole LiNC isomer (broken line) for both approaches to symmetry of the quasi-linear species LiNC and LiCN (non-linear C_s, linear $C_{\infty v}$).

the discrepancies can also be interpreted from the point of view of deviations from the RRHO model. In a completely anharmonic and non-rigid treatment there should not be significant differences between the situations depicted as C_s and $C_{\infty v}$ (for sufficiently small deviations from linearity). With respect to the quality of the RRHO treatment, it should also be mentioned that for quasi-linear species the conventional rotational partition function may not work well at low temperatures. Overall, of the two approaches presented, C_s and $C_{\infty v}$, the $C_{\infty v}$ data should represent a better, more reliable evaluation of the system characteristics. Because, according to the computational results [1–14], the LiCN system is a rather non-rigid, fluxional system [35–37], its treatment within a whole potential hypersurface is desirable (i.e. one super-species treatment); however, this remains a remote possibility. It is clear that such fluxional species require more sophisticated partition functions; our treatment represents the current computational limit. Employing all the available information on the system and suggesting a logical completion of the results [13,14], it provides a useful evaluation of the possible effects. Moreover, there are arguments [18] that for non-rigid and anharmonic species a cancellation mechanism can still operate for the characteristics treated here (especially the w_i weight factors). Finally, the reported results refer to the situation of thermodynamic inter-isomeric equilibrium which need not be reached in an observation.

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REFERENCES

1 B. Bak, E. Clementi and R.N. Kortzeborn, J. Chem. Phys., 52 (1970) 764.
2 E. Clementi, H. Kistenmacher and H. Popkie, J. Chem. Phys., 58 (1973) 2460.
3 V.A. Istomin, N.F. Stepanov and B.I. Zhilinskii, J. Mol. Spectrosc., 67 (1977) 1977.
4 J.W. Bats and D. Feil, Chem. Phys., 26 (1977) 79.
5 A.I. Boldyrev, O.P. Charkin, K.V. Bozhenko, N.M. Klimenko and N.G. Rambidi, Zh. Neorg. Khim., 24 (1979) 612.
6 P. George, M. Trachtman and C.W. Bock, Int. J. Quantum Chem., 17 (1980) 599.
7 L.T. Redmon, G.D. Purvis III and R.J. Bartlett, J. Chem. Phys., 72 (1980) 986.
8 A. Schmiedekamp, C.W. Bock and P. George, J. Mol. Struct., 67 (1980) 107.
9 R. Essers, J. Tennyson and P.E.S. Wormer, Chem. Phys. Lett., 89 (1982) 223.
10 M.S. Gopinathan and C. Ravimohan, Chem. Phys. Lett., 85 (1982) 307.
11 G. Brocks and J. Tennyson, J. Mol. Spectrosc., 99 (1983) 263.
12 O.P. Charkin, D.G. Musaev and N.M. Klimenko, Koord. Khim., 11 (1985) 445.
13 P.v.R. Schleyer, A. Sawaryn, A.E. Reed and P. Hobza, J. Comput. Chem., 7 (1986) 666.

14 L. Adamowicz and C.I. Frum, Chem. Phys. Lett., 157 (1989) 496.
15 Z.K. Ismail, R.H. Hauge and J.L. Margrave, J. Chem. Phys., 57 (1972) 5137.
16 K. Nakamoto, D. Tevoult and S. Tani, J. Mol. Struct., 43 (1978) 75.
17 J.J. van Vaals, W.L. Meerts and A. Dymanus, Chem. Phys., 82 (1983) 385.
18 Z. Slanina, Contemporary Theory of Chemical Isomerism, Academia and Reidel, Prague and Dordrecht, 1986.
19 Z. Slanina, Int. Rev. Phys. Chem., 6 (1987) 251.
20 Z. Slanina, Thermochim. Acta, 128 (1988) 157.
21 R.J. Bartlett, Ann. Rev. Phys. Chem., 32 (1981) 359.
22 L. Adamowicz and R.J. Bartlett, J. Chem. Phys., 86 (1987) 6314.
23 L. Adamowicz, R.J. Bartlett and A.J. Sadlej, J. Chem. Phys., 88 (1988) 5749.
24 L. Adamowicz, Chem. Phys. Lett., 153 (1988) 147; 156 (1989) 628.
25 L. Adamowicz, J. Phys. Chem., 93 (1989) 1780.
26 K.S. Pitzer, J. Chem. Phys., 8 (1940) 711.
27 S.S. Zimmerman and H.A. Scheraga, Biopolymers, 16 (1977) 811.
28 M. Vásquez, G. Némethy and H.A. Scheraga, Macromolecules, 16 (1983) 1043.
29 L. Piela, G. Némethy and H.A. Scheraga, J. Am. Chem. Soc., 109 (1987) 4477.
30 Z. Slanina, Int. J. Quantum Chem., 16 (1979) 79.
31 Z. Slanina, Adv. Mol. Relaxation Processes, 14 (1979) 133.
32 Z. Slanina, Adv. Quantum Chem., 13 (1981) 89.
33 Z. Slanina, J. Phys. Chem., 92 (1988) 5836.
34 G.J. Mains, J.W. Larson and L.G. Hepler, J. Phys. Chem., 88 (1984) 1257.
35 R.S. Berry, in R.G. Woolley (Ed.), Quantum Dynamics of Molecules, Plenum, New York, 1980.
36 J. Jellinek and D.H. Lie, Phys. Rev. Lett., 62 (1989) 241.
37 D.H. Lie and J. Jellinek, Z. Phys. D, 12 (1989) 177.