The search for a possible twist phase transition in a biphenyl analogue: heat capacity of crystalline tolane

Kazuya Saito, Mayuko Asahina, Yasuhisa Yamamura and Isao Ikemoto

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan

Abstract. The heat capacity of crystalline tolane (diphenylacetylene) has been measured by adiabatic calorimetry between 9 and 303 K in order to see any phase transitions like those found in a similar compound, biphenyl. No thermal anomaly has been detected. The phonon dispersion relation of the compound is calculated using a simple model and compared with that of biphenyl. It is shown that the absence of a phase transition in crystalline tolane is consistent with the calculated dispersion relation. A certain height of the potential barrier at the planar conformation in the intramolecular potential for twisting motion is essential for the lattice instability of crystalline biphenyl. Some smoothed thermodynamic quantities are tabulated.

1. Introduction

Biphenyl (C_6H_5–C_6H_5), the first member of the so-called p-polyphenyls (H–$(C_6H_4)_n$–H, $n = 2, 3, \ldots$), is well known as an interesting compound that shows incommensurate phase transitions closely related to the molecular twisting degree of freedom [1–3]. The crystals of other members of the p-polyphenyls, which are isostructural to crystalline biphenyl, also show a similar phase transition associated with the molecular twisting [1]. Much attention has been paid to the compounds for clarifying the mechanism of the transitions from the molecular level. It is, nowadays, commonly accepted that the nature of the phase transitions in crystalline p-polyphenyls is determined by the delicate balance between the intramolecular potential and the intermolecular interaction. The modification of the intramolecular potential by chemical modification of the molecules, indeed, affects systematically the properties of the twist phase transition as revealed through the studies on fluorine substituted p-polyphenyls [4–8]. In this context, it is interesting to see what occurs if the potential energy curve for the twisting motion is essentially determined by only the intermolecular interaction.

For the purpose, the title compound, tolane (diphenylacetylene, C_6H_5–C≡C–C_6H_5), seems most suitable. The molecular structure is very similar to biphenyl and only twisting degrees of freedom can possibly be assumed as soft intramolecular motional degrees of freedom. The long distance between two benzene rings significantly reduces the steric repulsion between *ortho* hydrogen atoms and the triple bond between two central carbon atoms has effective axial symmetry. These make the potential curve very flat. Spectroscopic studies [9] have revealed that the potential curve is well decribed by a sinusoidal function with a period of π rad and a barrier height of 2.4 kJ mol^{-1} (200 cm^{-1}), which give an energy splitting of only 17 cm^{-1} for the lowest levels, ignoring the tunnel splitting. The location

of the minimum in the potential curve, however, has not been established experimentally [10]. For the biphenyl molecule, the barrier height is about 10 kJ mol^{-1} and the stable conformation is twisted [1, 2].

Tolane molecules crystallize into the monoclinic system with the space group $P2_1/c$ [10–15]. The crystal of tolane consists of two kinds of molecule, crystallographically independent. Both the molecules lie on inversion centres, resulting in a completely planar conformation. Since no appreciable intramolecular potential exists in the isolated state for the molecular twisting, the planar conformation in the crystalline state is forced by the intermolecular interaction.

Although some efforts have been expended to detect any manifestation of a possible phase transition, no success has been reported [15]. The search for a low-temperature phase transition made, however, has been limited to above liquid nitrogen temperature. The normal-incommensurate phase transition temperature, which is the 'twist' transition and the highest among three phase transitions in crystalline biphenyl, is 40.4 K [16, 17], far below the lower limit of the previous search. These situations prompted the present authors to start a search for a possible phase transition below liquid nitrogen temperature. The experimental technique employed is adiabatic calorimetry, which is sensitive enough to detect a small thermal anomaly and has no selection rule. In the present paper, the experimental results, including the thermodynamic functions obtained by the numerical integration of the data, are described. The absence of a twist transition is rationalized through a lattice dynamics calculation under a rigid and a flexible (semirigid) molecular model. The resulting phonon dispersion curves are compared with the curve reported previously for crystalline biphenyl [3] to shed light on the importance of the existence of a substantial potential barrier (of an isolated molecule) for the planar conformation in the phase transition of the biphenyl crystal. The usefulness of simple model calculations of the phonon dispersion relation is emphasized for the prediction of some lattice instability of (rather complicated) molecular crystals.

2. Experimental details

Commercially available tolane (Aldrich Chemical, Inc.) was purified further by fractional sublimation in vacuum around 310 K. The purified specimen was melted once under helium atmosphere at reduced pressure (10 kPa), cooled gradually for recrystallization, and then pulverized. The powdered sample was loaded into the calorimeter vessel and sealed with a small amount of helium gas (8 kPa at room temperature) to assist quick thermal equilibration in the measurements. The amount of the sample used for measurements was 2.3945 g (0.013 435 mol) after the buoyancy effect had been corrected for. The sample contributed more than 30 per cent of the total heat capacity that consists of the contributions of the sample and of the calorimeter vessel.

Details of the apparatus and the operation of the adiabatic calorimeter have been described elsewhere [8]. Platinum (Minco Products, Inc., S1055) and germanium (Lake-Shore Cryotronics Inc., GR-200B-500) resistance thermometers were mounted on the calorimeter vessel and used above and below 13.8 K, respectively. Although the temperature scales of both the thermometers are based on the ITS-90, a small discontinuity in the temperature dependence of the heat capacity is detected in typical measurements including the present experiment.
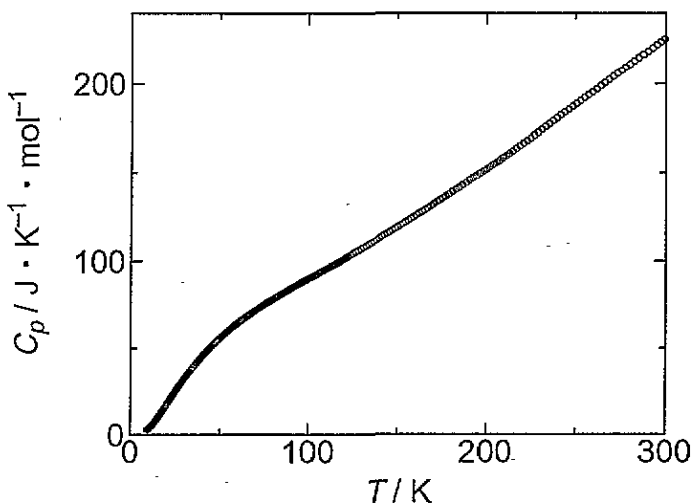
Figure 1. Measured molar heat capacities of crystalline tolane.

3. Results and discussion

Measured molar heat capacities of crystalline tolane are plotted in figure 1 for the whole temperature range studied. There is nothing anomalous in the temperature dependence. The time required for thermal equilibration within the calorimeter vessel after each energy input was within the range of 1–7 min depending smoothly on the temperature and is quite normal in comparison with previous measurements on several samples [5, 7, 8]. Temperature drift was a slowly varying function of temperature throughout the measurement. It is therefore concluded that crystalline tolane undergoes neither phase transition nor glass transition below room temperature. These conclusions are consistent with the structural investigation [15], which did not detect any disorder or large-amplitude motion. The upper limit of the entropy of transition, if present, is estimated to be smaller than 0.1 J K^{-1} mol^{-1}.

Some thermodynamic functions of the solid state were estimated by graphical integration of the experimental heat capacity curve, and are given in table 1 at rounded temperatures. In the integration, a small contribution below 10 K was estimated by extrapolating the curve smoothly to follow the Debye rule in the low-temperature limit. It is noted that calculation of the statistical entropy is impractical for the present compound because of the lack of the reliable data of molecular vibrations [18–20] as is common for very flexible molecules.

It is interesting to see the phonon dispersion relations of crystalline tolane, because the dispersion relation of the room-temperature (high-temperature) phase of the biphenyl crystal clearly shows a manifestation of the incommensurate lattice modulation at low temperatures [3]. The phonon dispersion relation of crystalline tolane is calculated within the atom–atom potential approximation using the Buckingham-type interatomic potential function, the parameters of which are taken from the literature [21]. Only a twisting degree of freedom is included in the calculation within the flexible (or semirigid) molecular model, in addition to translational and rotational degrees of freedom of a rigid body. The total number of degrees of freedom is seven in the flexible molecular model and six in the rigid molecular model. The molecule is assumed to consist of two benzene rings connected by the central –C≡C– moiety. Benzene rings are assumed to be normal hexagons with C–C bond-length of 1.397 Å. Hydrogen atoms are assumed to lie 0.995 Å outward from the bonding carbon

Table 1. Molar thermodynamic quantities of tolane.

T K	C_p J K^{-1} mol^{-1}	$[H(T) - H(0)]/T$ J K^{-1} mol^{-1}	$S(T) - S(0)$ J K^{-1} mol^{-1}	$-[G(T) - G(0)]/T$ J K^{-1} mol^{-1}	T K	C_p J K^{-1} mol^{-1}	$[H(T) - H(0)]/T$ J K^{-1} mol^{-1}	$S(T) - S(0)$ J K^{-1} mol^{-1}	$-[G(T) - G(0)]/T$ J K^{-1} mol^{-1}
10	3.55	0.95	1.27	0.32	160	125.68	71.44	140.15	68.71
15	9.77	2.78	3.79	1.01	170	132.09	74.82	147.96	73.14
20	17.33	5.46	7.62	2.16	180	138.62	78.18	155.70	77.51
30	32.48	11.98	17.55	5.57	190	145.35	81.54	163.37	81.83
40	45.40	18.77	28.73	9.96	200	152.22	84.90	171.00	86.10
50	55.99	25.20	40.04	14.84	210	159.21	88.27	178.60	90.32
60	64.49	31.06	51.03	19.96	220	166.34	91.66	186.17	94.51
70	71.69	36.36	61.52	25.16	230	173.60	95.06	193.72	98.66
80	78.18	41.19	71.52	30.33	240	181.00	98.49	201.26	102.77
90	84.28	45.64	81.09	35.45	250	188.40	101.94	208.80	106.87
100	90.04	49.80	90.27	40.47	260	195.81	105.41	216.34	110.93
110	95.76	53.71	99.12	45.40	270	203.30	108.89	223.87	114.97
120	101.49	57.45	107.69	50.24	280	210.86	112.40	231.40	119.00
130	107.40	61.07	116.05	54.98	290	218.42	115.92	238.93	123.00
140	113.29	64.59	124.22	59.64	298.15	224.55	118.81	245.07	126.26
150	119.38	68.04	132.25	64.21	300	225.93	119.47	246.46	126.99

atoms in the plane of the benzene ring. The bonds, C–C≡C–C, are assumed linear with the bond-lengths of 1.426 and 1.212 Å for the single and the triple bonds, respectively. Before the lattice dynamics calculation, the crystal structure is optimized within the experimental space group to establish the consistency. In the structure optimization and the lattice dynamics calculation, the intramolecular force acting on the intramolecular twisting degree of freedom is assumed to be negligible.
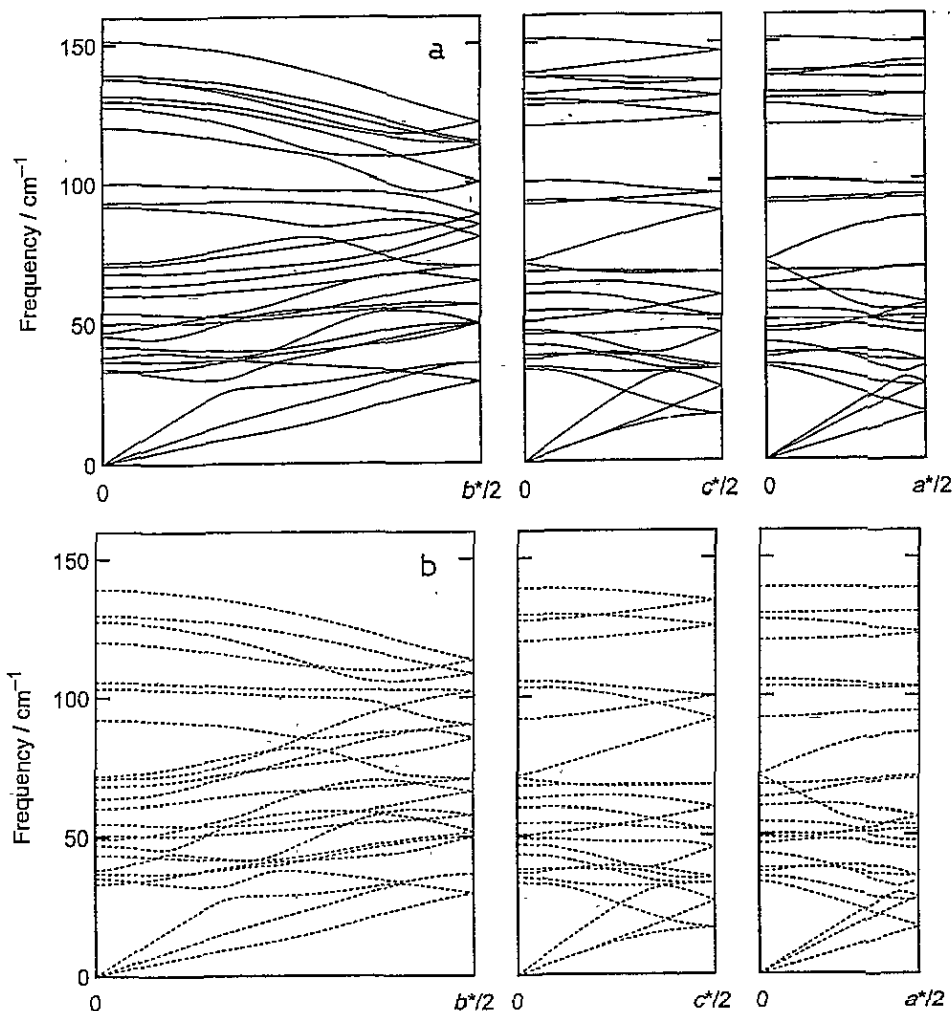

Figure 2. Phonon dispersion relations of crystalline tolane within the flexible (a) and the rigid (b) molecular models.

The phonon dispersion relations obtained within the flexible and the rigid molecular models are shown in figure 2. There is no apparent dip (minimum) in the lowest branches in either of the models. This behaviour is very different from the phonon dispersion relations of the high-temperature phases of crystalline biphenyl [3], p-terphenyl (C_6H_5–C_6H_4–C_6H_5 or H–$(C_6H_4)_3$–H) [22] and bis(4-chlorophenyl)sulphone (($ClC_6H_4)_2SO_2$) [23], all of which undergo structural phase transitions, closely related to their intramolecular twisting degrees of freedom. In the case of biphenyl, the soft mode is known as the lowest branch

characterized with the wavevector around the dip in the dispersion relation [1, 3]. As for the dispersion relation of *p*-terphenyl calculated under some pressure [22], a fluorine-substituted analogue, the 4,4″-difluoro-*p*-terphenyl (F–$(C_6H_4)_3$–F) crystal under normal pressure, which is believed being to be in some respects to crystalline *p*-terphenyl under pressure, shows *an incommensurate phase transition with the wavevector roughly corresponding to the minimum in the dispersion relation* [5, 6, 8]. An incommensurate phase transition occurs also in crystalline bis(4-chlorophenyl)sulphone [24–26], where the structural modulation in the low-temperature incommensurate phase [27] agrees well, though qualitatively, with the eigenvector components of the lowest branch at the dip [23]. The absence of any distinct minimum in the dispersion relation of the lowest branches of crystalline tolane, therefore, seems very consistent with the fact that no phase transition occurs. A similar situation can be found also for 4,4′-difluorobiphenyl (F–$(C_6H_4)_2$–F) [4, 28, 29], which does not undergo a twist transition in contrast to the unsubstituted compound, biphenyl. These situations show, in a sense, the usefulness of a simple model calculation, such as that employed in the present study, of the phonon dispersion relation of a high-temperature phase for prediction of lattice instability in (rather complicated) molecular crystals, which possibly causes a displacive phase transition.
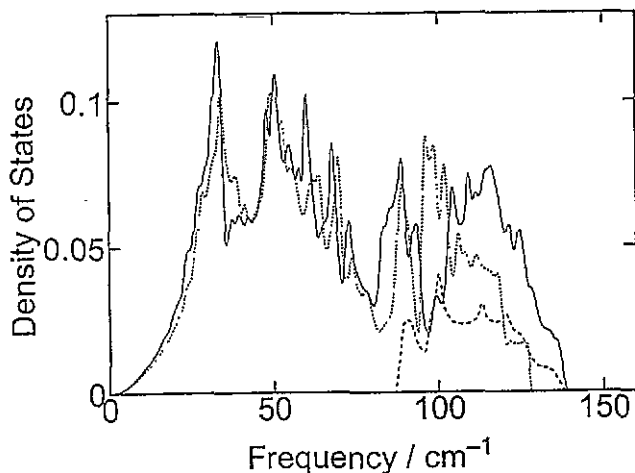

Figure 3. Phonon density of states of crystalline tolane calculated within the flexible (solid line) and the rigid (dotted line) molecular models. That obtained from the calculation incorporating only the twisting degree of freedom is shown by a dashed line for comparison.

From the comparison of the dispersion relations within the flexible and the rigid molecular models, it is evident that inclusion of the twisting degrees of freedom hardly affects the low-frequency part, though a coupling between the twisting and the lattice degrees of freedom is clear from the phonon density of states in figure 3. Four new branches appear above 90 cm^{-1} as in figure 2 when the twisting degrees of freedom are included in the calculation. The essential features are the same if the dispersion curves are calculated while taking only the twisting degree of freedom into account in the calculation. These situations are also different from the case of biphenyl, where, according to Plakida *et al* [3], bare twisting modes lie about 50 cm^{-1}, resulting in strong coupling with an acoustic branch. Since the motion of the benzene rings in tolane molecules is governed by only the intermolecular interaction in the present treatment, the origin of the rather high frequency of the twisting branches is from them. The contribution from the intermolecular interaction

to the force field that determines the twisting motion should be positive in both tolane and biphenyl crystals, because crystals are unstable against twisting type deformation unless this is the case. As the moment of inertia for the twisting motion is the same in tolane and biphenyl, the difference in the frequency can be roughly said to be due to the difference in the intramolecular contribution to the force field. Indeed the stable conformation in the isolated state is twisted about 40°, in contrast to the planar conformation in the room-temperature (high-temperature) phase of biphenyl [1, 2]. This means the intramolecular contribution to the force field is definitely negative. In contrast, a small, positive or negative, contribution is expected for an isolated tolane molecule from the spectroscopic results [9]. It is evident that the inclusion of such a small intramolecular contribution does not alter the situation because the frequencies should show small (irrelevant to the discussion) shifts starting from the present result. The existence of the barrier at the planar conformation, or, in other words, the competition between the intra- and the intermolecular interaction is, therefore, essential for the occurrence of the structural phase transitions in crystalline biphenyl.

4. Conclusion

The heat capacity of crystalline tolane, an analogue of biphenyl, was measured from 9 K to 303 K, in order to see any phase transition closely related to the molecular twisting degrees of freedom known in crystalline *p*-polyphenyls. No thermal anomaly attributable to any phase transition was detected. Simple lattice dynamics calculation incorporating only a twisting degree of freedom showed no manifestation of lattice instability that could possibly cause a displacive phase transition. The absence of a symptom of lattice instability is consistent with the experimental finding of no phase transition. From the comparison of the resulting dispersion relations and those for crystalline biphenyl reported before [3], it is shown that the competition between the intra- and the intermolecular interaction in biphenyl molecule is essential for the structural phase transitions in crystalline biphenyl.

Simple lattice dynamics calculations on high-temperature phases give a reasonable prediction concerning a possible displacive phase transition associated with lattice instability in several molecular crystals, as pointed out in the discussion. It is therefore concluded that such a treatment is useful for prediction of lattice instability in (rather complicated) molecular crystals.

References

[1] Cailleau H, Baudour J L, Meinnel J, Dworkin A, Moussa F and Zeyen C M E 1980 *Faraday Discuss. Chem. Soc.* **69** 7
[2] Cailleau H 1985 *Incommensurate Phases in Dielectrics 2 Materials* (Amsterdam: North-Holland) ch 12
[3] Plakida N M, Belushkin A V, Natkaniec I and Wasiutynski T 1983 *Phys. Status Solidi* b **118** 129
[4] Saito K, Atake T and Chihara H 1987 *Acta Crystallogr.* B **43** 383
[5] Saito K, Yamamura Y, Saitoh H, Matsuyama H, Kikuchi K and Ikemoto I 1993 *Solid State Commun.* **87** 903
[6] Saitoh H, Saito K, Yamamura Y, Matsuyama H, Kikuchi K and Ikemoto I 1993 *Solid State Commun.* **91** 89
[7] Saito K, Yamamura Y, Saitoh H, Matsuyama H, Kikuchi K and Ikemoto I 1994 *Solid State Commun.* **92** 495
[8] Yamamura Y, Saito K, Saitoh H, Matsuyama H, Kikuchi K and Ikemoto I 1995 *J. Phys. Chem. Solids* **56** 107
[9] Okuyama K, Hasegawa T, Ito M and Mikami N 1984 *J. Phys. Chem.* **88** 1711
[10] Abramenkov A V, Almenningen A, Cyvin B N, Cyvin S J, Jonvik T, Khaikin L S, Rømming C and Vilkov L V 1988 *Acta Chem. Scand.* A **42** 674
[11] Robertson J M and Woodward I 1938 *Proc. R. Soc.* A **164** 436
[12] Samarskaya V D, Myasnikova R M and Kitaigorodskii A I 1968 *Krystallografiya* **13** 616
[13] Mavridis A and Moustakali-Mavridis I 1977 *Acta Crystallogr.* B **33** 3612

[14] Espiritu A A and White J G 1978 *Z. Krystallogr.* **147** 177

[15] Zanin I E, Antipin M Yu and Struchkov Yu T 1991 *Sov. Phys.–Crystallogr.* **36** 219

[16] Atake T and Chihara H 1980 *Solid State Commun.* **35** 131

[17] Atake T, Saito K and Chihara H 1983 *Chem. Lett.* 493

[18] Kellerer B and Hacker H H 1972 *J. Mol. Struct.* **13** 79

[19] Baranovic' G and Colombo L 1986 *J. Mol. Struct.* **147** 275

[20] Palmö K 1988 *Spectrochim. Acta* A **44** 341

[21] Williams D E 1967 *J. Chem. Phys.* **47** 4680

[22] Wasiutynski T and Cailleau H 1992 *J. Phys.: Condens. Matter* **4** 6241

[23] Saito K, Kikuchi K and Ikemoto I 1992 *Solid State Commun.* **81** 241

[24] Corbero J M, Pusiol D J, Wolfenson D E and Brunetti A H 1985 *Phys. Status Solidi* a **91** K97

[25] Kasano H, Koshiba T, Kasatani H and Terauchi H 1990 *J. Phys. Soc. Japan* **59** 408

[26] Etrillard J, Even J, Sougoti M, Launois P, Longeville S and Toudic B 1993 *Solid State Commun.* **87** 47

[27] Zuniga F J, Pélez-Mato J M and Breczewski T 1993 *Acta Crystallogr.* B **49** 1060

[28] Saito K, Atake T and Chihara H 1986 *J. Chem. Thermodyn.* **18** 407

[29] Wasicki J, Belushkin A V, Khomenko V G, Natkaniec I, Telezhenko Yu V and Wasiutynski T 1988 *Phys. Status Solidi* b **145** 445