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A Mean-Square Displacement Amplitude Analysis of Terminally Bound CO Groups in Transition-Metal Clusters

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Abstract

Mean-square displacement amplitudes (m.s.d.a.'s) obtained from conventional room-temperature and low-temperature X-ray diffraction, and from neutron diffraction studies of metal carbonyl clusters are analyzed for the terminally bound CO groups. The relationships between m.s.d.a.'s of M, C and O atoms are investigated by applying the 'rigid-body' test along the M–C, M–O and C–O vectors, and are examined on the basis of simple vibrational motion models. Results of this analysis show that the C-atom m.s.d.a.'s are substantially affected by bonding electron density deformation. The relationship with the 'sliding effect' observed on passing from isotropic to anisotropic treatment of the C-atom thermal motion is also discussed.

Introduction

Carbon monoxide as a ligand plays a central role in metal cluster chemistry and certainly represents one of the most studied molecules in the organometallic field. The extraordinary geometrical versatility shown by CO is demonstrated in the results of scores of structural studies on metal carbonyl complexes and clusters both in solution and in the solid state (Band & Muetterties, 1978; Evans, 1977). As a matter of fact, while spectroscopic techniques have provided most information on the dynamic processes related to CO fluxionality in solution (Adams & Cotton, 1985), thus far solid-state aspects of CO structural chemistry mainly have been investigated by single-crystal X-ray and neutron diffraction (Raithby, 1980). More recently the borderline between static and dynamic implications of CO structural chemistry has become more and more narrow as migrational processes have been claimed to occur for some metal carbonyl clusters in the solid state (mainly by solid state NMR techniques) (Hanson, Lisic, Petty & Iannacone, 1986; Hanson & Lisic, 1986) and X-ray solid-state data have in turn been used to provide correlations with dynamic processes occurring in solution (Benfield & Johnson, 1980; Braga & Heaton, 1987). Moreover, the availability of large amounts of both experimental and theoretical informa-

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tion has rendered comparative structural analyses aimed towards structural rationalizations particularly appealing (Crabtree & Lavin, 1986).

However, recently it has been shown that great attention must be paid when speculations on the CO-ligand stereogeometry are based on solid-state data obtained from conventional single-crystal X-ray studies of metal carbonyl clusters (Braga & Koetzle, 1987). It has been observed that the C-atom position (and to a lesser extent the O-atom position) of a terminally bound CO group strongly depends on the model employed in the crystallographic refinement. In fact, a systematic and significant 'sliding' of the C atoms towards the O atoms was observed on simply passing from isotropic to anisotropic refinement of the light-atom displacement parameters.

The results of a study on the mean-square displacement amplitudes ('thermal' parameters; m.s.d.a.'s hereafter) for a series of metal cluster species containing only or mainly terminal CO's are now reported. This study lends further support to the observation made previously that the C atoms in such systems present an electron density distribution which cannot be appropriately described by the spherical atom model used in conventional X-ray diffraction work.

The method

The method applies to the mean-square displacement amplitudes ('thermal' parameters) obtained from single-crystal X-ray and neutron diffraction studies and is based on the 'rigid-body' test proposed by Rosenfield, Trueblood & Dunitz (1978), which is a generalization of the 'rigid-bond' postulate formulated by Hirshfeld (1976). The initial proposition was that torsional and angle-bending deformations to a large extent dominate the intramolecular motions in the solid state, while very little contribution usually comes from bond-stretching vibrations when covalently bonded atoms are considered. Thereafore the m.s.d.a.'s of a pair of rigidly bonded atoms of comparable masses evaluated along the bond direction are, in principle, equivalent for the two atoms. The extension of this postulate to non-bonded atoms within the same molecule leads to the 'rigid-body' or 'rigid-molecule' test mentioned above. In the other words, if the quantity Δ_{A-B} is defined as the difference, calculated along the interatomic direction, between the m.s.d.a.'s of two atoms A and B (Δ_{A-B} = m.s.d.a.$_A$–m.s.d.a.$_B$), the condition $\Delta_{A-B} \cong 0$ should be satisfied if the rigid-bond/-body model is appropriate for the two atoms. On the other hand it has been shown that when the rigid-bond test fails for covalently bonded atoms (thus leading to a value of $\Delta_{A-B} \neq 0$) the displacement parameters may be affected by charge-density deformation contributions (or other systematic errors) (Hirshfeld, 1976).

In these cases the displacement parameters tend to 'cover up' for chemical bond features and do not represent pure atomic thermal vibrations.

Conversely, when the rigid-bond test is satisfied, but specific parts of a molecule show large deviations from rigid-body behaviour (thus causing extensive disagreement between observed displacement parameters and those calculated on the basis of the rigid model); indications of intramolecular preferred motions can also be obtained (Rosenfield, Trueblood & Dunitz, 1978; Chandrasekhar & Bürgi, 1984; Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979).

Results and discussion

Using this approach, a number of data sets coming from both our own experimental work on metal carbonyl cluster species and from the literature were evaluated as test cases.

At this stage it should be mentioned that the main limitation to this kind of analysis was found to be the very availability of the vibrational parameters, not only because they are rarely reported, but also because, even when obtainable from published papers, they often contain numerical errors or lack correct specification of the temperature-factor exponent form.

Data were grouped in the following four categories depending on the type of refinement and on whether X-ray or neutron diffraction had been employed:

(a) Conventional X-ray data collected at room temperature.

(b) X-ray data collected at low temperature, normal refinement.

(c) X-ray data collected at low temperature, structure refinement based on high-order data.

(d) Neutron data (low temperature).

Results of the computations are reported in Tables 1 and 2, together with references. For all calculations the THMA10 program was used (Trueblood, 1986).

For each structure determination, only terminally bound CO groups were taken into account, regardless of the molecular geometry or of the presence of other ligands bonded to the metallic framework. Three distinct Δ_{A-B} values (m.s.d.a. atom A minus m.s.d.a. atom B) were calculated for each CO group: Δ_{O-C}, which relates the two light atoms; and Δ_{C-M} and Δ_{O-M}, which relate the two light atoms to the metal atom M (see Fig. 1). These values were then averaged over all equivalent CO groups within the same molecule ($\langle \Delta \rangle$), and r.m.s. deviations $\{\sigma(\Delta)=[(\sum \Delta^2-n\bar{\Delta}^2)/n]^{1/2}$, where $\bar{\Delta} = \sum \Delta/n\}$ were computed for each mean value (see tables). Separate mean values were calculated when independent molecules were present in the unit cell or when sets of non equivalent CO's were present as in the case of mixed-metal species.

It should be emphasized that the prerequisites of the Hirshfeld (1976) rigid-bond postulate are satisfied only

Table 1. *Values of* $\langle \Delta_{A-B} \rangle$ ($\text{Å}^2 \times 10^4$) *from conventional and low-temperature X-ray data*

	$\langle \Delta_{C-M} \rangle$	$\langle \Delta_{O-C} \rangle$	$\langle \Delta_{O-M} \rangle$	$(\sin\theta/\lambda)_{max}$ (Å^{-1})	N_{obs}	N_{var}	R/wR	T (K)	Ref.
(a) Conventional X-ray data									
[Rh$_6$C(CO)$_{13}$][PPh$_4$]$_2$	110 (43)	−46 (41)	70 (43)	0·44	4286	513	0·029/0·032	RT	1
	127 (23)	−69 (34)	64 (21)	0·64	8207	513	0·034/0·037	RT	
[Rh$_6$C(CO)$_{15}$\{Cu(PPh$_3$)\}$_2$]	114 (20)	−64 (27)	55 (9)	0·54	6326	447	0·029/0·031	RT	2
[Co$_3$C(CO)$_9$]$_2$	113 (21)	−75 (35)	42 (16)	0·54	1843	199	0·019/0·021	RT	3
[Co$_6$C(CO)$_{15}$][N(C$_2$H$_5$)$_4$]$_2$	175 (75)	−155 (90)	43 (32)	0·44	2997	523	0·058/0·061	RT	4
	124 (16)	−76 (45)	53 (34)	0·70	5963	523	0·063/0·066	RT	
[(PPh$_3$)RuCo(CO)$_6$(μ-PPh$_2$)]*									
'Ru(CO)$_3$'	101 (82)	−45 (59)	58 (28) ⎫	0·44	4225	206	0·037/0·041	RT	5
'Co(CO)$_3$'	148 (21)	−116 (17)	35 (22) ⎭						
'Ru(CO)$_3$'	101 (20)	−56 (20)	46 (6) ⎫	0·60	5668	206	0·037/0·039	RT	
'Co(CO)$_3$'	105 (11)	−70 (26)	37 (16) ⎭						
[Ru$_3$(CO)$_{12}$]	102 (17)	−47 (18)	69 (20)	0·50	2281	†	0·026/0·028	RT	6
[Os$_3$(CO)$_{12}$]	131 (41)	−81 (76)	61 (34)	0·54	3040	245	0·033/0·036	RT	7
(b) Low-temperature X-ray data, normal refinement									
[HFeCo$_3$(CO)$_9$\{P(OMe)$_3$\}$_3$]‡									
'Fe(CO)$_3$'	94 (17)	−50 (14)	44 (7)	0·70	6057		0·061/0·067	134	8
3 'Co(CO)'	92 (35)	−61 (49)	31 (14)						
[Ir$_3$(CO)$_7$(μ-PPhCH=CHPPh$_2$)]	116 (56)	−63 (92)	68 (25)	0·63	4535		0·038/0·041	238	9
[HFe$_3$(CO)$_9$(CH,C=NH)]	61 (11)	−24 (14)	35 (10)	0·76	4849		0·029/0·042	115	10
[HFe$_3$(CO)$_9$(N=CHCH$_3$)]	75 (19)	−57 (19)	53 (31)	0·70	3260		0·041/0·048	115	10
[Fe$_3$(μ-CO)$_2$(CO)$_6$(μ-CMe)(C$_5$H$_5$)]	108 (42)	−49 (44)	59 (34)	0·57	2286		0·039/0·038	153	11

References: (1) Braga & Heaton (1987); (2) Albano, Braga, Fumagalli & Martinengo (1987); (3) Albano & Braga (unpublished); (4) Martinengo, Strumolo, Chini, Albano & Braga (1985); (5) Braga (unpublished); (6) Churchill, Hollander & Hutchinson (1977); (7) Churchill & DeBoer (1977); (8) Huie, Knobler & Kaesz (1978); (9) Rafalko, Watson, Malueg, Davis & Gates (1981); (10) Andrews, van Buskirk, Knobler & Kaesz (1979); (11) Rybin, Petrovskaya, Struchkov, Batsanov & Rybinskaya (1982).

* Values calculated for the two independent 'M(CO)$_3$' units present in the molecule.
† Not reported.
‡ One 'Fe(CO)$_3$' and three 'Co(CO)' units present in the structure.

Table 2. *Values of* $\langle \Delta_{A-B} \rangle$ ($\text{Å}^2 \times 10^4$) *from high-order X-ray and neutron data*

	$\langle \Delta_{C-M} \rangle$	$\langle \Delta_{O-C} \rangle$	$\langle \Delta_{O-M} \rangle$	$(\sin\theta/\lambda)_{min}$ (Å^{-1})	$(\sin\theta/\lambda)_{max}$ (Å^{-1})	N_{obs}	N_{var}	R/wR	T (K)	Ref.
*(a) High-order X-ray data**										
[Mn$_2$(CO)$_{10}$]	21 (7)	6 (2)	20 (5)	0·76	1·32	4583†	—	0·14/0·07	74	1
[Co$_2$(CO)$_8$]‡	17 (7)	7 (5)	23 (5) ⎫	0·60	1·04	3426	175	0·076/0·087	100	2
	28 (4)	6 (1)	26 (5) ⎭							
[Co$_2$(CO)$_6$(^{t}Bu$_2$C$_2$)]	12 (7)	14 (11)	19 (7)	0·85	1·00	2811	217	0·042/0·043	122	3
*(b) Neutron data**										
[HFeCo$_3$(CO)$_9$\{P(OMe)$_3$\}$_3$]§										
'Fe(CO)$_3$'	19 (10)	13 (10)	15 (3) ⎫		0·68	8229	—	0·087/0·066**	90	4
3 'Co(CO)'	16 (18)	11 (10)	12 (6) ⎭							
[H$_3$Os$_3$(CO)$_9$(μ_3-CH)]¶	16 (3)	6 (4)	15 (5) ⎫		0·68	4962	—	0·022/0·022	11	5
	16 (4)	6 (3)	15 (3) ⎭							
[HFe$_4$(CO)$_{12}$(η^2-CH)]¶	18 (10)	11 (12)	20 (11) ⎫		0·61	5663	—	0·066/0·079**	26	6
	18 (9)	17 (11)	15 (9) ⎭							
[Co$_3$(CO)$_9$CH]	10 (9)	5 (4)	11 (6)		0·80	3781	210	0·037/0·022	102	7

References: (1) Martin, Rees & Mitschler (1982); (2) Leung & Coppens (1983); (3) Baert, Guelzim, Poblet, Wiest, Demuynck & Benard (1986); (4) Teller, Wilson, McMullan, Koetzle & Bau (1978); (5) Orpen & Koetzle (1984); (6) Beno, Williams, Tachikawa & Muetterties (1981); (7) Leung, Coppens, McMullan & Koetzle (1981).

* Absolute values of Δ_{A-B} were averaged.
† Number of reflections used for the full data-set refinement.
‡ Two independent 'half' molecules in the unit cell.
§ One 'Fe(CO)$_3$' and three 'Co(CO)' units present in the structure.
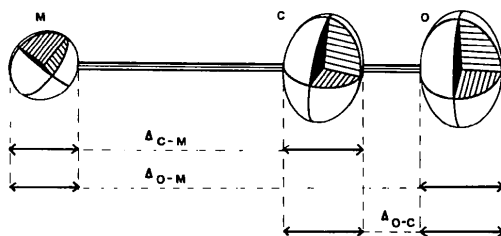¶ Two independent molecules in the unit cell.
** R values based on F^2.

Fig. 1. Representation of Δ_{A-B} values (m.s.d.a. atom A minus m.s.d.a. atom B) for a terminally bound CO group.

in the case of Δ_{O-C} which corresponds to differences in m.s.d.a.'s between covalently bonded atoms of equivalent mass; conversely Δ_{C-M} and Δ_{O-M} do not relate atoms of similar mass, nor does Δ_{O-M} represent a pair of bonded atoms. Nevertheless, the formalism is useful for the present analysis, which is aimed *only* at recognition of possible relationships between equivalent quantities calculated for the same entity (CO) in similar structural environments and evaluated with different crystallographic procedures. Moreover, a

preliminary screening of the data reported in Tables 1 and 2 shows that there is no effect related to the different metal-atom masses. The existence of systematic relationships between $\langle \Delta \rangle$ values can be easily detected by inspecting Table 1(a) where $\langle \Delta \rangle$ values for conventional room-temperature X-ray data are reported. These relationships can be summarized as follows:

(1) No $\langle \Delta \rangle$ value approaches zero – not even $\langle \Delta_{O-C} \rangle$ which is related to such a stiff entity as a triply bonded C—O.

(2) Moreover, $\langle \Delta_{O-C} \rangle$ appears to be always negative, thus implying that the vibrational component of the C atom along the C—O vector is always larger than that of the O atom.

(3) $\langle \Delta_{C-M} \rangle$ and $\langle \Delta_{O-M} \rangle$ are otherwise always positive thus implying that C and O motions along the M—O vector are larger than M motion.

(4) $\langle \Delta_{C-M} \rangle$ values are always much larger than both $\langle \Delta_{O-C} \rangle$ (in absolute value) and $\langle \Delta_{O-M} \rangle$ values. The relationship $\langle \Delta_{O-M} \rangle = \langle \Delta_{C-M} \rangle + \langle \Delta_{O-C} \rangle$ is roughly satisfied in all cases.

(5) Although the individual values of Δ are quite scattered and some of the $\sigma(\Delta)$'s are fairly large, these trends are never contradicted (we have rather found that poor quality X-ray data usually lead to loss of these relationships).

(6) No dependence on the metal-atom mass (as mentioned above) or on the $(\sin\theta/\lambda)_{max}$ value can be confidently envisaged.

Remarkably $\langle \Delta \rangle$ values taken from low-temperature X-ray work (Table 1b) exactly conform to the same relationships listed above, although all values appear to be slightly smaller than those of Table 1(a). Altogether what seems more difficult to work out on the basis of these figures is the reason for the inequalities $\langle \Delta_{O-C} \rangle < O$ and $\langle \Delta_{C-M} \rangle > \langle \Delta_{O-M} \rangle$, that is to say the reason why the C-atom displacements are larger than those of the O atoms along the bond axis. It is worth recalling that the major vibrational components for C and O atoms of terminally bound CO groups are always found to be roughly perpendicular to the ligand axis with larger displacements for the O than C atoms. This behaviour is in agreement with a simple picture of the CO vibrational motion as occurring mainly via M—C—O angle bending and libration of the group as a whole around a conic angle (see Figs. 2a,b). However these vibrational models (or their combination) do not seem able to rationalize larger displacements along the bond axis for the C atoms than for the O atoms with respect to the metal atoms.

The difficulty met in elaborating a convincing vibrational model may also be taken as indicative that C-atom displacement amplitudes are affected by a significant contribution from charge-density deformation around the C atom. This hypothesis was tested by applying a similar thermal-motion analysis to the experiments grouped in categories (c) and (d), which

are expected to be free from bonding electron density bias. As a matter of fact the influence of bonding electrons can be reduced by refining the nuclear positions based on high-order X-ray data (case c) which are dominated by core electrons (Angermund, Claus, Goddard & Krüger, 1985); or can be totally eliminated if neutron diffraction data are used (case d).

$\langle \Delta \rangle$ values are reported in Tables 2(a) and 2(b) for groups (c) and (d), respectively.

A substantial agreement between $\langle \Delta \rangle$ values for both high-order X-ray data and neutron data can be noticed immediately. Moreover $\langle \Delta_{C-M} \rangle$ and $\langle \Delta_{O-M} \rangle$ show very similar values, while $\langle \Delta_{O-C} \rangle$ truly conform to the Hirshfeld postulate, giving values very close to zero.

The case of $[HFeCO_3(CO)_9\{P(OMe)_3\}_3]$ is certainly very indicative: the marked difference between $\langle \Delta_{C-M} \rangle$ and $\langle \Delta_{O-M} \rangle$ present in the X-ray results, though the data were collected at low temperature (134 K), completely disappears in the neutron results (90 K), thus strengthening the idea that the behaviour observed when full X-ray data sets are employed is mainly due to extensive bonding-electron contributions which are convoluted in the C-atom displacement parameters.

Relationship with the 'sliding' effect and conclusions

As mentioned above the C atoms of terminally bound CO groups were found to 'slide' along the $M\cdots O$ vectors towards the O atoms on simply passing from isotropic to anisotropic refinement of the light atoms, yielding a significant difference in M—C and C—O bond lengths between the two kinds of treatments (Braga & Koetzle, 1987). It was in fact observed that a general lengthening of the M—C distances was accompanied by an equivalent shortening of C—O leaving the $M\cdots O$ separation almost unaltered. Bond-length differences between the isotropic and anisotropic models were of the order of 0·02–0·05 Å and were found to decrease with the increase of the limiting value, $(\sin\theta/\lambda)_{max}$, adopted for data collection. However, coincidence could not be achieved even with fairly large data sets
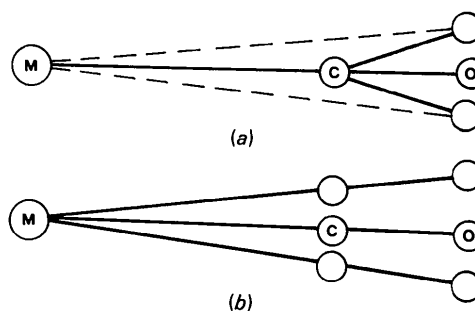

Fig. 2. Schematic representation of intramolecular motions for a terminally bound CO group. Broken and solid lines indicate 'soft' and 'rigid' interactions according to the inequalities: (a) $\Delta_{O-M} > \Delta_{C-M}$ bending; (b) $\Delta_{O-M} = \Delta_{C-M}$ libration.

$[(\sin\theta/\lambda)_{max} < 0.70 \text{Å}^{-1}]$. No dependence on the metal-atom mass was detected.

Both the absence of any mass effect related to the type of metal atoms and the fact that only (or mainly) the C atoms are involved seem to suggest some sort of relationship between the 'sliding' effect and the anomalies shown by the C-atom m.s.d.a. values (or, at least, the existence of a common cause underlying two different phenomena). As a matter of fact both 'sliding' and m.s.d.a. values may be considered to reflect the deviation of the electron density distribution around the C-atom nuclei from the ideal spherical atom model, arising from the bonding interaction established by the CO molecule in these systems.

In other words the model fitted on the observed non-spherical electron density distribution around the C atom is progressively 'adjusted' on passing from a spherical atom allowed to vibrate isotropically (*i.e.* spherically) to a spherical atom allowed to describe an anisotropic thermal ellipsoid, which ends up compensating for the use of an inappropriate scattering function. The contamination of the vibrational motion by bonding electron density contribution is then reflected both by the gross violation of the Hirshfeld postulate for C≡O even at low temperature and by the peculiar relationship between $\langle \Delta_{C-O} \rangle$, $\langle \Delta_{C-M} \rangle$ and $\langle \Delta_{O-M} \rangle$ values taken from full X-ray data-set refinements. It is worth mentioning, at this stage, that charge-density maps reported for species such as $[Cp(CO)_2Fe]_2$ (Mitschler, Rees & Lehmann, 1978), $[Mn_2(CO)_{10}]$ (Martin, Rees & Mitschler, 1982) and $[Cr(CO)_6]$ (Rees & Mitschler, 1976) invariably show that M—C bonding peaks, along the M—C—O axis, appear to be higher than the O-atom lone pairs. This common feature may provide an explanation for $\langle \Delta_{O-C} \rangle$ being negative, because m.s.d.a.'s for C atoms will be artificially higher to account for the two M—C and C—O bonding peaks, while the lower lone-pair density for O atoms will have less effect of the O-atom m.s.d.a.'s.

However the phenomenon may be more complicated: for instance a librational motion component, implying swinging of the whole CO group against rather 'soft' M—C interactions, and which is frozen out by decreasing the temperature, cannot be completely ruled out on the basis of the data discussed here. Collection of large X-ray data sets at different temperatures, comparison with neutron data and aspherical atom refinements on well-suited test cases should be carried out in order to assess the true nature of the phenomenon.

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Structure and Steric Hindrance Analyses to Determine the Dynamical Disorder in 1-Iodoadamantane (C₁₀H₁₅I)

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Abstract

A structure determination was undertaken to obtain a precise description of the disorder in the high-temperature phase of 1-iodoadamantane at 295 and 256 K. The compound crystallizes in the orthorhombic system (space group $Pmmn$) with $Z = 2$ [parameters at $T = 256$ K: $a = 8.640$ (17), $b = 6.693$ (13), $c = 8.854$ (17) Å, $V = 512.0$ Å^3, $D_x = 1.70$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 31.05$ cm^{-1}, $F(000) = 256$, $R = 3.54$, $wR = 3.75\%$ for 1211 observed reflections $(F_{obs} > 6\sigma_F)$]. The crystal was grown from a solution in methanol. The best refinements were obtained with either independent atoms or a rigid group in a Frenkel-model framework ($R \simeq 4\%$). These two models led to similar results but did not settle definitively the number and location of the molecular equilibrium positions. The relatively high values of the **TLS** components compared with those found for other adamantane derivatives are typical of a dynamical disorder corresponding to uniaxial molecular jumps. A steric hindrance analysis showed unambiguously that the molecule occupies two discernible equilibrium positions, the molecular mirror lying on the (010) crystal one. The two equilibrium positions are related to each other by a rotation of 60° around the C_3 molecular axis. The antiparallel arrangement of the molecular dipole axis leads to an antiferroelectric order in the distorted pseudocubic lattice, and may be compared with the local order in the glassy phase of 1-cyanoadamantane.

Introduction

This work is part of a systematic study of crystalline substituted adamantanes. Structure determination, NMR, IQNS and dielectric relaxation experiments lead to a better understanding of the properties of different phases: the molecular arrangement, dynamical disorder and phase transitions are strongly dependent on the substitution and electric dipole moment of the molecule.

1-Haloadamantanes (halo = F, Cl, Br) and 1-cyanoadamantane crystallize in a cubic plastic phase at room temperature or above and in (semi-) ordered phases at low temperature (Clark, McKnox, Mackle & McKervey, 1977). We report here on 1-iodoadamantane, which undergoes a first-order solid–solid transition at $T_t = 211$ K and melts at $T_m = 347$ K (Clark, McKnox, Mackle & McKervey, 1977).

Differential scanning calorimetry and studies on a polarizing microscope equipped with a heating stage have not revealed any plastic phase in 1-iodoadamantane (Cuvelier & Foulon, 1986). Partial structural results and NMR studies (Virlet, Quiroga, Boucher, Amoureux & Castelain, 1983) induced a model of quasi-free uniaxial rotation described by four discernible positions corresponding to 30° molecular jumps around the dipolar axis with an associated relaxation time $\tau_{m12} = 1.7 \times 10^{-12}$ s at 295 K.

The low activation energy (5.1 kJ mol^{-1}), deduced from the Arrhenius law [$\tau_{m12} = 2.1 \times 10^{-13}$ exp $(5.1/RT)$], leads to the assumption of weak steric hindrance. In the present paper, we shall re-examine the orientational disorder and try to compare the structure of 1-iodoadamantane with those of other substituted adamantanes.

Experimental

The title compound was purified by successive sublimations and recrystallizations in methanol. Crystals were obtained by slow evaporation in methanol. Single crystals were sealed in a glass capillary to prevent sublimation and mounted on a Philips PW 1100 automatic diffractometer equipped with a nitrogen gas flow Nonius device.

Many of the crystals presented a growth twin in which the two individuals were related by a symmetry with respect to the ($\bar{1}$10) plane (Fig. 1*a*). The smaller individuals gave rise to extra Bragg reflexions in the reciprocal lattice of the larger ones (Fig. 1*b*). Measurement of the non-overlapping ones permitted evaluation of the relative volumes of the two individuals (5 and 95% respectively of the total crystal). Moreover, some of the extra Bragg reflexions can be indexed as ($h/2$, $k/2$, l) in the reciprocal lattice of the larger individual. This could have lead to an incorrect determination of the cell parameters and/or could have been interpreted as a superstructure in the local order.