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LETTERS

First isolation of tautomeric isomers of 4-isopropyltropolone as inclusion complex crystals

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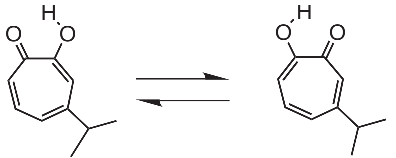
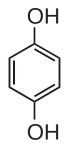
Abstract—Tautomeric isomers of 4-isopropyltropolone have been isolated as inclusion complex crystals and their crystal structures have been elucidated by X-ray analyses. © 2001 Elsevier Science Ltd. All rights reserved.

Tropolone derivatives have received considerable attention in recent years as dynamic molecular systems for intramolecular proton tunneling and/or proton transfer.[1] The electronic and steric effects of substituents on the tautomerism of tropolone derivatives have been studied by infrared,[2] Raman,[3] NMR[4] and laser fluorescence excitation[5] spectroscopies. However, isolation of the tautomeric isomers of tropolone derivatives has never been reported. Here, we report the first isolation of two distinct isomers of 4-isopropyltropolone (**1a** and **1b**) as inclusion complex crystals (**I**–**III**) with the host compounds (**2**–**4**).



1a **1b**



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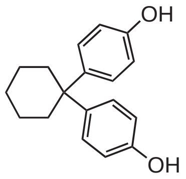

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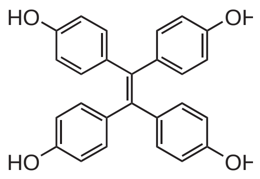

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I: 1:1 inclusion complex of **2** with **1b**
II: 1:1 inclusion complex of **3** with **1b**
III: 1:2 inclusion complex of **4** with **1a**

Keywords: tautomeric isomers; inclusion crystals; 4-isopropyltropolone; X-ray structures.

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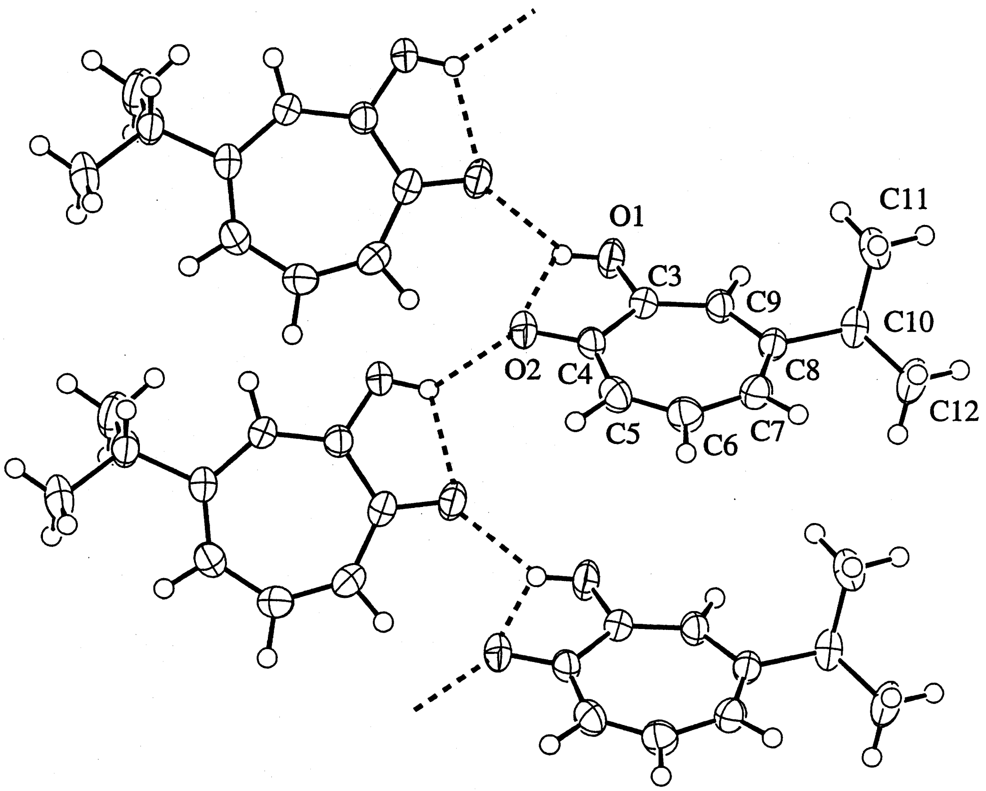

Figure 1. Chain structure of **1a** formed by the bifurcated hydrogen bond around the twofold screw axis.

When a solution of 4-isopropyltropolone **1** (1.0 g, 6.09 mmol) and hydroquinone **2** (0.67 g, 5.99 mmol) in ether (10 ml) was kept at room temperature for 12 h, a 1:1 inclusion compound (**I**) of **2** and **1b** was obtained as pale yellow plate-like crystals (0.84 g, 51% yield, mp 84–86°C). 1,1-Di(4-hydroxyphenyl)cyclohexane host **3** also formed a 1:1 inclusion crystal (**II**) of **3** and **1b** as colorless prisms (mp 110–113°C), while the host compound **4**[6] formed a 1:2 inclusion crystal (**III**) of **4** and **1a** as colorless needles (mp 149–151°C). The host–guest ratios of the inclusion crystals (**I**–**III**) were determined by NMR and elemental analysis, and confirmed by X-ray analyses.

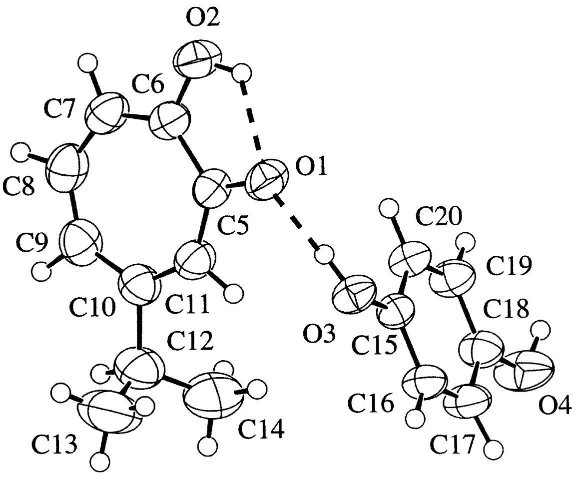

Figure 2. Ellipsoid representation (50%) of (**I**).

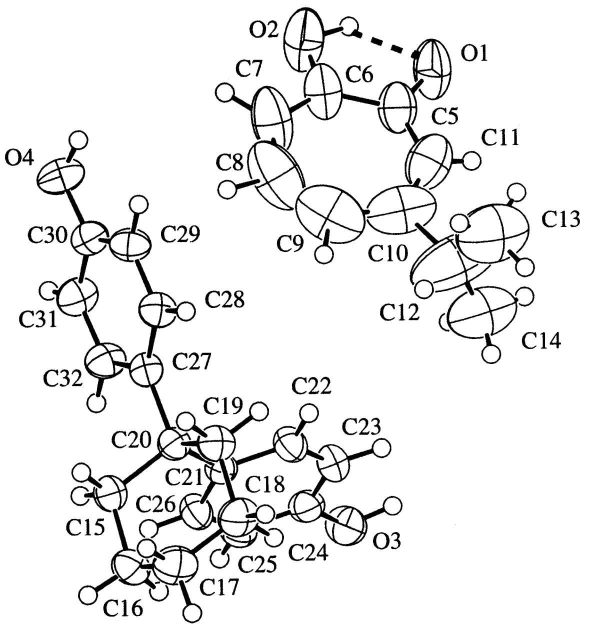

Figure 3. Ellipsoid representation (50%) of (**II**).

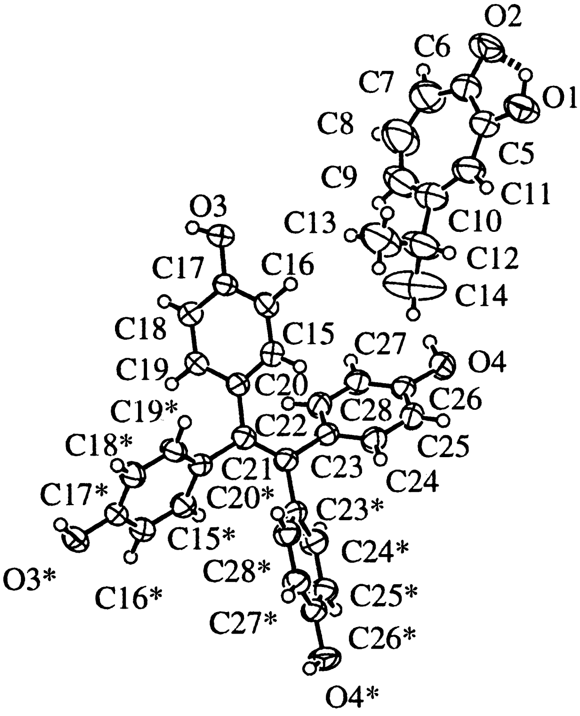

Figure 4. Ellipsoid representation (50%) of (**III**).

The crystal structure of **1** has been redetermined in the present study to amend the positional parameters of the hydroxyl H atom reported previously.[7] As shown in Fig. 1, the keto and hydroxyl O atoms of **1a** are arranged around the crystallographic twofold screw axis to form a chain structure by the bifurcated hydrogen bond. X-Ray crystal structure analyses of the inclusion compounds, (**I**–**III**), have also been carried out.[8] Molecular structures of (**I**–**III**) are shown in Figs. 2–4, respectively. The bond distances in the tropolone ring indicate typically an alternation of the short and long bonds (Table 1). In these crystals, the guest molecule acts as both a hydrogen acceptor at the keto O atom and a donor of a bifurcated hydrogen bond at the hydroxyl group to form hydrogen bonds with the host molecules. In (**I**), the host molecules **2** form a zigzag chain along the *c* axis by the O4–H4···O3(x, y, z+1) hydrogen bond (Fig. 5). The guest **1b** connects the two chains of the host by the hydrogen bonds [O3–H3···O1, and O2–H2···O3(−x, 1−y, −z)]. In (**II**), host molecules **3** form a chain along the *a* axis by the O4–H4···O3(x+1, y, z) hydrogen bond (Fig. 6). The guest **1b** connects the two chains of the host by the hydrogen bonds [O3–H3···O1(1−x, 1−y, −z), and O2–H2···O4(2−x, 1−y, 1−z)]. In (**III**), the central C–C bond of the host **4** lies on a twofold axis parallel to *b*, and the host

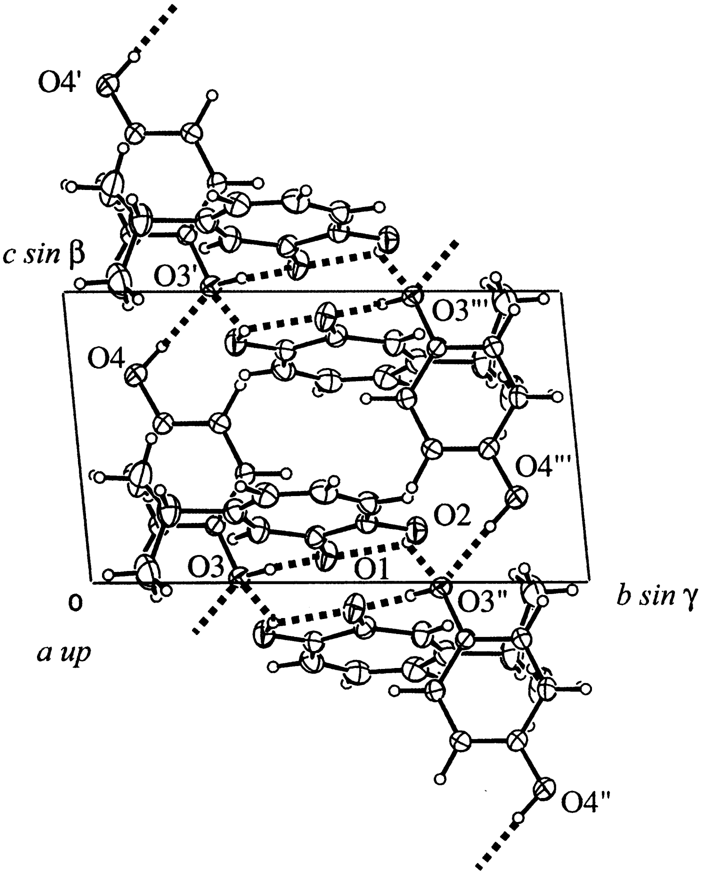

Figure 5. Projection of the crystal structure of (**I**) along *a*. Triclinic, *P*-1, *Z*=2.

Table 1. Bond distances (Å) in tropolone moiety

1a		**(I)**		**(II)**		**(III)**	
O1–C3	1.339(2)	O1–C5	1.262(2)*	O1–C5	1.262(3)*	O1–C5	1.334(4)
O2–C4	1.255(2)*	O2–C6	1.332(2)	O2–C6	1.339(3)	O2–C6	1.252(4)*
C3–C4	1.466(3)	C5–C6	1.462(3)	C5–C6	1.441(3)	C5–C6	1.452(4)
C3–C9	1.372(3)*	C5–C11	1.418(2)	C5–C11	1.432(4)	C5–C11	1.366(4)*
C4–C5	1.419(2)	C6–C7	1.365(3)*	C6–C7	1.359(4)*	C6–C7	1.411(6)
C5–C6	1.366(3)*	C7–C8	1.396(3)	C7–C8	1.383(5)	C7–C8	1.361(6)*
C6–C7	1.409(3)	C8–C9	1.363(3)*	C8–C9	1.316(7)*	C8–C9	1.405(6)
C7–C8	1.363(2)*	C9–C10	1.403(3)	C9–C10	1.406(6)	C9–C10	1.349(7)*
C8–C9	1.418(2)	C10–C11	1.370(2)*	C10–C11	1.387(6)*	C10–C11	1.383(5)

*These distances correspond to the formal double bonds in the tautomer.

molecules form a chain along the *b* axis by the O3–H3···O4(*x*, *y*–1, *z*) hydrogen bond (Fig. 7). The guest **1a** connects the two chains of the host by the hydrogen bonds [O4–H4···O2(3/2–*x*, 1/2–*y*, 1–*z*), and O1–H1···O3(3/2–*x*, 1/2+*y*, 1/2–*z*)].

In the crystals of **1**, the molecules **1a** form a chain structure as shown in Fig. 1. If they were the **1b** tautomer, the isopropyl group would be bonded to the C6 atom, which is closer to the center of the hydrogen bond chain than the C8 atom, and some intermolecular repulsion might be caused. It seems that the packing efficiency including the hydrogen bonds determines the tautomeric structure of the guest molecule in the inclusion compounds, i.e. **1a** in (**III**), and **1b** in (**I**–**II**).

Acknowledgements

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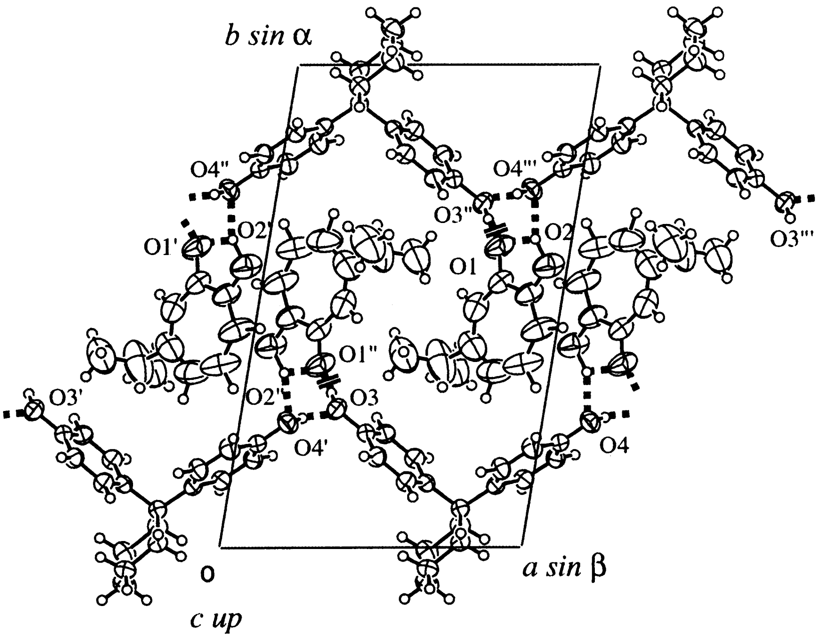

Figure 6. Projection of the crystal structure of (**II**) along *c*. Triclinic, *P*-1, *Z*=2. Dashed lines represent hydrogen bonds. The symbol --‖-- indicates that the two lines --| and |-- are parallel but heights are different.

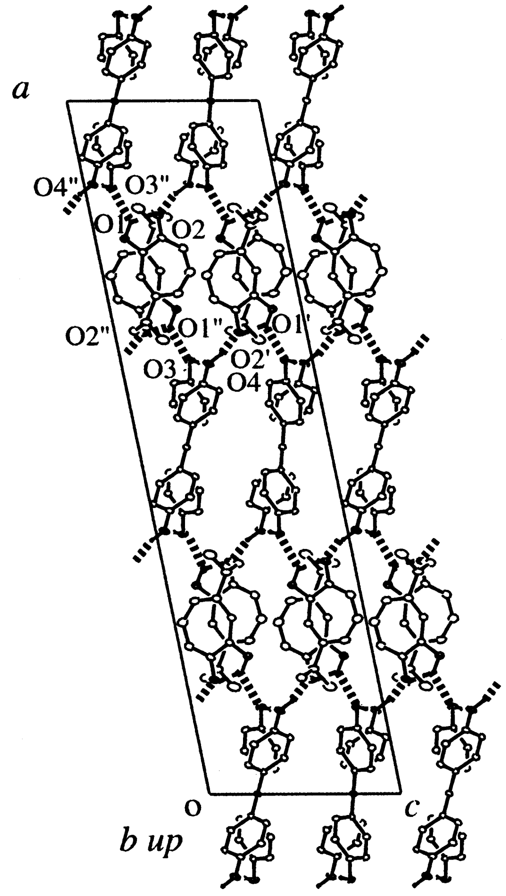

Figure 7. Projection of the crystal structure of (**III**) along *b*. Monoclinic, *C*2/*c*, $Z=4$.

References

1. Frost, R. K.; Hagemeister, F. C.; Arrington, C. A.; Schleppenbach, D.; Zwier, T. S.; Jordan, K. D. *J. Chem. Phys.* **1996**, *92*, 2790.
2. Ikegami, Y. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1118.
3. Ikegami, Y. *Bull. Chem., Res. Inst. Non-Aqueous Solutions, Tohoku Univ.* **1967**, *17*, 45.
4. Sugiyama, H.; Ito, S.; Nozoe, T. *Tetrahedron Lett.* **1965**, 179.
5. Tsuji, T.; Hamada, H.; Hayashi, Y.; Sekiya, H.; Mori, A.; Nishimura, Y. *J. Chem. Phys.* **1999**, *110*, 966.
6. Tanaka, K.; Fujimoto, D.; Altreuther, A.; Oeser, T.; Irngartinger, H.; Toda, F. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2115.
7. Ohishi, H.; Tsujibo, H.; Inoue, M.; Inamori, Y. *Acta Crystallogr., Sect. C* **1994**, *50*, 587.
8. Crystal data for **1a**: $C_{10}H_{12}O_2$, crystal dimensions 0.50×0.50×0.45 mm^3, colorless, measured on a Rigaku AFC-7R diffractometer with Cu Kα radiation at 250 K; monoclinic *C*2/*c*, $a=23.064(5)$, $b=6.452(1)$, $c=15.961(4)$ Å, $\beta=132.73(1)°$, $V=1744.6(7)$ Å^3, $Z=8$, $D_x=1.250$ Mg m^{-3}, $\mu=0.696$ mm^{-1}, data collection of 1961 reflections ($\lambda_{max}=75°$), 1712 independent reflections ($R_{int}=0.075$), 1672 observed reflections with $I>2\sigma(I)$, 158 parameters (All H-atom parameters refined). $R(F)=0.043$ for 1672 observed reflections, $wR(F^2)=0.115$ for all the 1712 reflections. Crystal data for (**I**): $C_6H_6O_2 \cdot C_{10}H_{12}O_2$, crystal dimensions 0.6×0.5×0.2 mm^3, pale yellow, measured on a Rigaku AFC-7R diffractometer with Mo Kα radiation at 298 K; triclinic *P*-1, $a=9.605(3)$, $b=12.117(3)$, $c=7.0956(9)$ Å, $\alpha=100.18(1)$, $\beta=107.38(2)$, $\gamma=72.50(2)°$, $V=748.2(3)$ Å^3, $Z=2$, $D_x=1.218$ Mg m^{-3}, $\mu=0.087$ mm^{-1}, data collection of 3640 reflections ($\lambda_{max}=27.5°$), 3438 independent reflections ($R_{int}=0.02$), 2525 observed reflections with $I>2\sigma(I)$, 254 parameters (All H-atom parameters refined). $R(F)=0.055$ for 2525 observed reflections, $wR(F^2)=0.170$ for all the 3438 reflections; Crystal data for (**II**): $C_{18}H_{20}O_2 \cdot C_{10}H_{12}O_2$, crystal dimensions 0.6×0.6×0.2 mm^3, colorless, measured on a Rigaku AFC-7R diffractometer with Mo Kα radiation at 298 K; triclinic *P*-1, $a=10.913(3)$, $b=17.578(2)$, $c=6.4055(8)$ Å, $\alpha=94.85(1)$, $\beta=98.64(1)$, $\gamma=79.96(1)°$, $V=1194.0(4)$ Å^3, $Z=2$, $D_x=1.203$ Mg m^{-3}, $\mu=0.079$ mm^{-1}, data collection of 5773 reflections ($\lambda_{max}=27.5°$), 5483 independent reflections ($R_{int}=0.006$), 4034 observed reflections with $I>2\sigma(I)$, 390 parameters (H-atom parameters refined except for those of isopropyl group of the guest). $R(F)=0.053$ for 4034 observed reflections, $wR(F^2)=0.159$ for all the 5483 reflections. Crystal data for (**III**): $C_{26}H_{20}O_4 \cdot (C_{10}H_{12}O_2)_2$, crystal dimensions 0.45×0.2×0.2 mm^3, orange, measured on a Rigaku AFC-7R diffractometer with Mo Kα radiation at 298 K; monoclinic *C*2/*c*, $a=38.510(2)$, $b=10.117(3)$, $c=10.420(4)$ Å, $\beta=101.45(1)°$, $V=3979(2)$ Å^3, $Z=4$, $D_x=1.210$ Mg m^{-3}, $\mu=0.082$ mm^{-1}, data collection of 4833 reflections ($\lambda_{max}=27.5°$), 4570 independent reflections ($R_{int}=0.027$), 2169 observed reflections with $I>2\sigma(I)$, 306 parameters (H-atom parameters refined except for those of isopropyl group of the guest). $R(F)=0.055$ for 2169 observed reflections, $wR(F^2)=0.183$ for all the 4570 reflections; CCDC 150506–CCDC 150509.