Very long C–H···O contacts can be weak hydrogen bonds: experimental evidence from crystalline $[Cr(CO)_3\{\eta^6\text{-}[7\text{-}\mathit{exo}\text{-}(C\equiv CH)C_7H_7]\}]$

Thomas Steiner,*[a] Bert Lutz,[b] John van der Maas,[b] Antoine M. M. Schreurs,[c] Jan Kroon[c] and Matthias Tamm*[d]

[a] *Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany*

[b] *Department of Analytical Molecular Spectrometry, Faculty of Chemistry, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands*

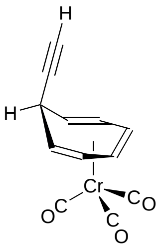
[c] *Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

[d] *Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstraße 34-36, D-14195 Berlin, Germany*

The crystal structure of the title compound contains a very long C–H···O contact from the ethynyl group to a carbonyl ligand with a H···O separation of 2.92 Å; weakly hydrogen bonding character of this contact is inferred from the Raman and the IR absorption spectra, showing the long range nature of the C–H···O hydrogen bond.

Terminal alkynes are among the best studied donors of C–H···X hydrogen bonds.[1,2] This is because of two reasons: one is the high acidity and hence the strong donor potential, and one is the good and robust suitability for vibrational spectroscopic experiments.[3] In C–H···O hydrogen bonds donated by terminal alkynes, H···O separations are typically in the range 2.1–2.6 Å, with the mean value 2.37(4) Å.[1,4] If particularly strong acceptors like P=O are involved, H···O distances can be as short as 2.0 Å.[5] Whereas no conceptual problems arise for strong acceptors and short C≡C–H···O contacts, very little is known about long C–H···O (and more generally on long D–H···A) contacts. The open question is very simple: to which distances can C–H···O interactions be elongated before losing their hydrogen bond character? Currently, there seems to be consensus that no clear distance limits can be given, and that for increasing H···O and C···O separations, there is a gradual transition from hydrogen bond interactions to 'nothing'.[1] Still, the question remains: to which distances can physical effects of C–H···O interactions be detected, and when do the effects become more or less undetectable? In this contribution, we report structural and spectroscopic data on the longest alkynyl C–H···O contact discussed so far, which can still be reasonably regarded as a weak 'hydrogen bond'.

As part of our studies on ligands containing cycloheptatrienylium rings,[6] we prepared compound **1**.†



1

In terms of hydrogen bond potentials, the strongest donor in **1** is the ethynyl group and as hydrogen bond partners, there are the weak C≡C,[7] C=C[8] and CO[9] acceptors available. In this situation, it is impossible to predict which of the potentially resulting hydrogen bond types would eventually be formed in the solid state (if one is formed at all). In the crystal structure,‡ **1** is found in the expected conformation, Fig. 1(*a*). The shortest intermolecular contact of the ethynyl group is with a CO ligand of a neighboring molecule, Fig. 1(*b*). This contact is very long with H···O 2.92 Å (for C–H 1.08 Å) and C···O 3.71 Å, and the C–H···O angle is bent far from linearity, 130°.§ When looking only at the geometry, it is questionable how to interpret this contact: the distance is very long, much longer than van der Waals separation, the angle is strongly bent, and the CO ligand is one of the weakest O-acceptors known. No C–H···O contact of such a geometry has ever been clearly identified as a hydrogen bond. On the other hand, weak hydrogen bond nature has been shown for similarly long C≡C–H··π contacts,[7,8] suggesting this matter should be followed in further depth.

In vibrational spectroscopic experiments,¶ the alkynyl C–H stretching frequency $\nu_{\equiv C-H}$ was determined under a variety of sampling conditions in the crystalline state and in apolar solvents. This is to exclude possible matrix or solvent effects on $\nu_{\equiv C-H}$. Most important is the data on matrix-free polycrystalline **1** (determined by FT-Raman spectroscopy), which was obtained from small crystals taken without further sample treatment from

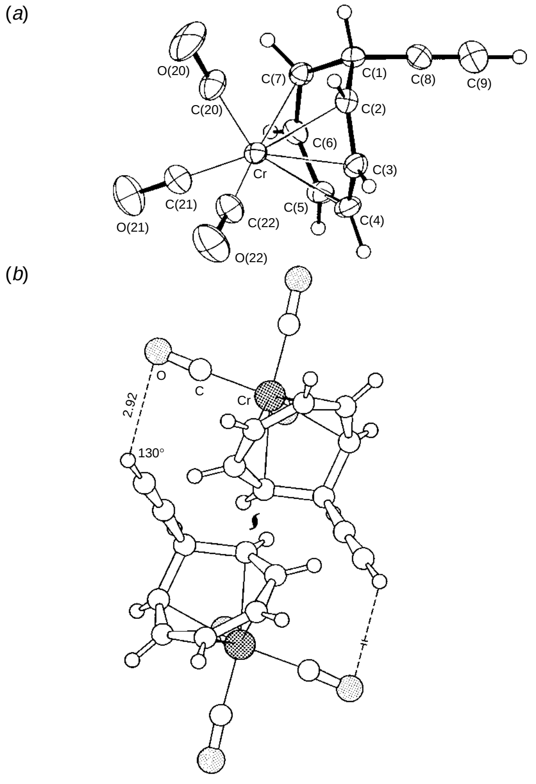


Fig. 1 (*a*) Molecular structure and atomic numbering scheme of **1**. (*b*) The very long C–H···O contact in crystalline**1**, numerical data is given for C–H 1.08 Å. The projection is along the screw axis of the space group; the apparently cyclic motif is therefore in fact a screw.

Table 1 IR alkynyl C–H stretching frequencies (cm^{-1}) of **1** in different environments

Sample of **1**	Spectrum	$\nu_{\equiv\mathrm{C-H}}$
Polycrystalline matrix-free	FT-Raman	3293
Polycrystalline in poflu-oil[a]	FTIR	3293
Polycrystalline in KBr	FTIR	3293
Solution in *n*-hexane	FTIR	3315
Solution in CCl_4	FTIR	3310

[a] Poly(chlorotrifluoroethylene).

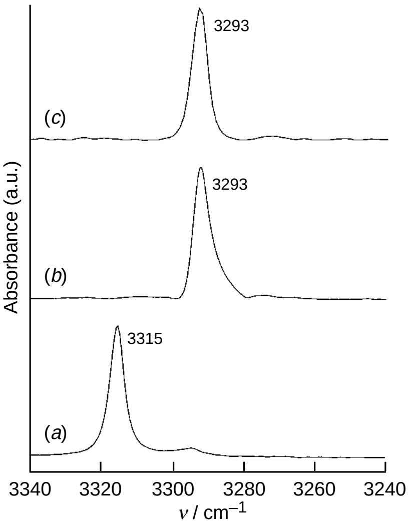


Fig. 2 Alkynyl C–H stretching region of the vibrational spectrum. (*a*) FT-Raman spectrum of a matrix-free polycrystalline sample. (*b*) FTIR spectrum of a polycrystalline sample in a poly(chlorotrifluoroethylene) mull. (*c*) FTIR spectrum of a dilute solution in *n*-hexane.

the same batch as the crystal used for X-ray data collection. FTIR spectra of polycrystalline samples in an inert mull and in KBr were also determined. All three $\nu_{\equiv\mathrm{C-H}}$ values are identical at 3293 cm^{-1} (Table 1 and Fig. 2), which is slightly but significantly reduced compared to the *ca.* 3315 cm^{-1} which are typical for 'free' alkynyl $\nu_{\equiv\mathrm{C-H}}$.[3] The identity of the three values under different sampling conditions makes matrix and sample preparation artifacts unlikely. Since $\nu_{\equiv\mathrm{C-H}}$ of 'free' molecules R–C≡C–H can slightly depend on the nature of R and also on the experimental conditions, IR absorption spectra were determined of dilute solutions in the apolar solvents *n*-hexane and CCl_4. The $\nu_{\equiv\mathrm{C-H}}$ values of 3315 and 3310 cm^{-1}, respectively, correspond to alkynyl groups which experience only very small (but necessarily non-zero) intermolecular interactions with 'inert' solvent molecules. The reduction of $\nu_{\equiv\mathrm{C-H}}$ in the crystalline state of *ca.* 20 cm^{-1} shows that in crystals, the alkynyl covalent C–H bond is slightly but detectably weakened owing to its intermolecular interactions. This bond weakening is an appropriate (and normally used[3]) indicator of C–H···X hydrogen bonding. A red-shift of 20 cm^{-1} is only a small effect. In 'normal' alkynyl C–H···O interactions, the corresponding red-shifts are in the range 40–100 cm^{-1}, and for strong C≡C–H···O=P hydrogen bonds, they can be 145 cm^{-1} and more.[3,5] This means that the intermolecular interactions in **1** do have an effect on the vibrational spectum, but this effect is small. We see no other interactions that the C–H···O contact that might be responsible, and therefore call it a 'weak hydrogen bond' (the terminologic classification, though, is of minor importance here).

The discussed contact with H···O 2.92 Å, is, to our knowledge, the longest C–H···O interaction for which effects on vibrational spectra have been experimentally shown. This is strong support for the long-range nature of C–H···O interactions, and clearly disfavours views that hydrogen bond character stops at the distance of the sum of van der Waals radii. On the other hand, one must consider that the red-shift of IR wavenumbers is only *ca.* 20 cm^{-1}, which is much smaller than for C–H···O interactions in optimal geometry: the strength of C–H···O hydrogen bonds at such distances is already very small. Since the donor studied here, C≡C–H, is stronger than most other C–H groups,[1] C–H···O contacts of similar geometries with less acidic C–H groups will be correspondingly weaker. We explicitly do not conclude that 'every C–H···O contact with H···O 2.9 Å is a hydrogen bond', but we state (based on experimental evidence) that such a contact can be a hydrogen bond.

T. S. thanks Professor W. Saenger for giving him the opportunity to carry out part of this work in his laboratory, and the Research Network of the European Union 'Molecular Recognition Phenomena' for supporting a stay in Utrecht. M. T. thanks the Deutsche Forschungsgemeinschaft (Ta 189/1-4,5) and the Fonds der Chemischen Industrie for financial support.

Footnotes and References

* E-mail: steiner@chemie.fu-berlin.de

† Complex **1**, tricarbonyl[η^6-(7-*exo*-ethynyl-1,3,5-cycloheptatriene)]-chromium(0), $[Cr(CO)_3\{\eta^6\text{-}[7\text{-}exo\text{-}(C{\equiv}CH)C_7H_7]\}]$, was prepared in 86% yield from $[Cr(CO)_3(C_7H_7)]BF_4$ and lithiated (trimethylsilyl)acetylene followed by desilylation in methanolic KOH. ^{1}H NMR ($CDCl_3$): δ 6.08 (m, 2 H), 5.91 (m, 2 H), 3.84 (t, 1 H, *endo*-H), 3.68 (m, 2 H), 2.09 (s, 1 H, C≡H). ^{13}C NMR ($CDCl_3$): δ 231.0 (CO), 98.9, 98.2 (C_7 CH), 83.8 (C≡CH), 71.2 (C≡CH), 60.3 (C_7 CH), 26.3 (C_7 C-7). Satisfactory C, H and N analyses were obtained.

‡ *Crystallography*: crystallisation from diethyl ether–hexane yields brown, block-shaped crystals. $C_{12}H_8CrO_3$, M = 252.2, monoclinic, space group $P2_1/c$ (no. 14), a = 10.367(1), b = 8.291(2), c = 13.135(2) Å, β = 95.93(1)°, U = 1120.1(3) Å^3, Z = 4, D_c = 1.495 g cm^{-3}, μ = 1.007 mm^{-1}. Enraf-Nonius FAST area detector, Mo-Kα radiation with λ = 0.710 73 Å, crystal dimensions 0.4 × 0.3 × 0.3 mm, room temp., 7779 reflections measured, 2569 independent (R_{int} = 0.062), 2025 with $I > 2\sigma(I)$, no absorption correction. Standard crystallographic computations[10,11] (refinement on F^2 of all reflections, H-atoms treated in the riding model with isotropic displacement parameter refined, 154 parameters vaired). Final R = 0.054 (for observed reflections), wR_2 = 0.119 (for all reflections). CCDC 182/689.

§ The second shortest contact of C≡C–H is to a CO ligand of a different neighbour with H···O 3.12 Å and C–H···O 109°.

¶ FT-NIR-Raman spectra were recorded of a matrix-free polycrystalline sample at room temp. (Perkin Elmer 2000 system, Nd/YAG laser, λ = 1064 nm, InGaAs detector, resolution 4 cm^{-1}, 128 scans). IR absorption spectra were recorded of polycrystalline **1** in a poly(chlorotrifluoroethylene) mull and in a KBr pellet, and of dilute solutions in *n*-hexane and in CCl_4 at room temp. (Perkin Elmer Model 2000 FTIR system, DTGS detector, optical resolution: 2 cm^{-1}; 8 scans, medium apodization, 0.5 mm KBr cells at concentrations < 0.5 mg ml^{-1}).

1 Th. Steiner, *Chem. Commun.*, 1997, 727.
2 G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441.
3 E. Steinwender, E. T. G. Lutz, J. H. van der Maas and J. A. Kanters, *Vib. Spectrosc.*, 1993, **4**, 217; B. Lutz, J. van der Maas and J. A. Kanters, *J. Mol. Struct.*, 1994, **325**, 203.
4 G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1990, 454.
5 Th. Steiner, J. van der Maas and B. Lutz, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1287.
6 M. Tamm, A. Grzegorzewski and I. Brüdgam, *J. Organomet. Chem.*, 1996, **519**, 217; M. Tamm, A. Grzegorzewski, Th. Steiner, W. Werncke and T. Jentzsch, *Organometallics*, 1996, **15**, 4984; M. Tamm, W. Werncke and T. Jentzsch, *ibid.*, 1997, **16**, 1418; M. Tamm, A. Grzegorzewski and Th. Steiner, *Chem. Ber./Recueil*, 1997, **130**, 225.
7 Th. Steiner, M. Tamm, A. Grzegorzewski, N. Schulte, N. Veldman, A. M. M. Schreurs, J. A. Kanters, J. Kroon, J. van der Maas and B. Lutz, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2441.
8 B. Lutz, J. A. Kanters, J. van der Maas, J. Kroon and Th. Steiner, *J. Mol. Struct.*, in press.
9 D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81.
10 G. M. Sheldrick, SHELXS86, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, pp. 175–189.
11 G. M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.

Received in Cambridge, UK, 26th September 1997; 7/06980D