

Structures and calculated NLO properties of (acenaphthylene)- and (acenaphthene)Cr(CO)₃

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Abstract

To be useful in elucidating structure–property relationships for the planar fused ring bearing metal π -complexation, the structures of (acenaphthylene)Cr(CO)₃ (**3**) and (acenaphthene)Cr(CO)₃ (**4**) were determined by X-ray crystal analyses, and their nonlinear optical activities investigated by using density functional theory calculations. The title molecules exhibit the intense electronic absorptions characteristic of charge-transfer capability and moreover, the observed negative solvchromicity in the low-energy transition is proposed to be associated with the organometallic modification of the electronic structure. These results are compared with the behavior of the corresponding free ligands, indicating that chromium tricarbonyl complexation can be used to create a unique non-centrosymmetric metal-organic architecture with the more extensive π -delocalization and, therefore, improve the nonlinear optical response.

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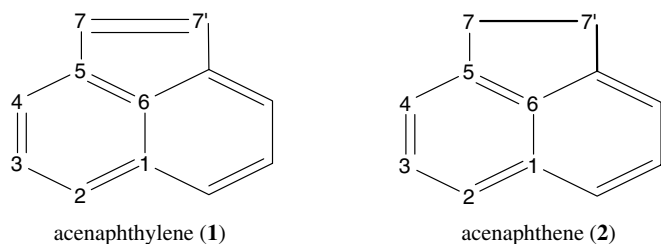
Keywords: Chromium tricarbonyl; Acenaphthylene; Acenaphthene; X-ray structure; Nonlinear optics

1. Introduction

The molecules with potential nonlinear optics (NLO) application are typically characterized by extensive π -electron conjugation, charge transfer ability, and acentric crystal structures. Recently there has been, and continues to be, a widespread interest in the organometallic and coordination complexes with improved material properties unobtainable in simple π -organic structures [1–7]. Frazier and co-workers [8] found in some, but not all (arene)Cr(CO)₃ complexes which exhibited solid-state second harmonic generation (SHG); they surmised that the other chromium compounds crystallized in centrosymmetric space groups, prohibiting them from creating the bulk polarity necessary to influence the incident light. Theoretical calculations from Kanis, Ratner and Marks (KRM) have shown that the wide range of electronic properties available to these organometallic structures would make it possible to fine

tune responses in nonlinear optical templates by judicious selection of the metal and the arene ligands [9]. These computational results are in agreement with the experiments performed by Müller and co-workers on the alkynyl- and alkenyl-bridged chromium carbonyl arene complexes [10]. Hinchliffe and co-workers have used density functional theory (DFT) method to study molecular polarizabilities of acenaphthylene (**1**) and acenaphthene (**2**) and give a prediction of asymmetric polarizability because of a great deal of strain in the five-membered ring [11]. The neutron diffraction studies of **1** and **2** appeared in the literature [12,13], but attempts to elucidate their detailed crystal structures by X-ray methods have been unsuccessful due to the high degree of disorder present in the structures at room temperature. Herein we are interested in determining how chromium tricarbonyl complexation can alter the electronic structure of polycyclic aromatic systems such as **1** and **2** and tune the NLO response. Although the syntheses of (acenaphthylene)Cr(CO)₃ (**3**) and (acenaphthene)Cr(CO)₃ (**4**) were previously reported [14,15], no prior structural data are available for them, and even very little is known

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Scheme 1. The organic ligands: acenaphthylene (1) and acenaphthene (2).

about their molecules from the electro-optic point of view. In this contribution, we wish to present the structures and NLO properties of **3** and **4**, together with those of their organic counterparts, **1** and **2**, for comparison. The chromium tricarbonyl substituent attached to acenaphthylene or acenaphthene plays an important role in the NLO enhancement (Scheme 1).

2. Experimental

2.1. General considerations

Unless otherwise noted, all manipulations were performed under an atmosphere of dry argon using standard Schlenk and vacuum techniques. All the solvents used were dried following standard methods. Absolute MeOH was used without purification and degassed before use. $\text{Cr}(\text{CO})_6$ (99% Aldrich) was sublimed prior to use. Acenaphthylene (95% Aldrich) and acenaphthene (98% Aldrich) were used as received. Elemental analyses were performed on an Elementar Vario EL III analyzer (C, H) and a TJARIS 1000 analyzer (Cr), respectively. Electron-impact Mass spectra were recorded on a Micromass GCT (EI, 70 eV) mass spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker AVANCE 500 MHz spectrometers using CDCl_3 as solvent and Me_4Si as internal standard. IR spectra were recorded on a Nicolet Magna-IR 550 instrument with KBr pellets. Column chromatography was performed on Matrix silica 60 (30–70 μm). UV–vis spectra were obtained on a Varian Cary 500 spectrophotometer rebuilt by OLIS to incorporate computer control. Measurements were made on argon saturated samples at 25 °C. Melting points were measured using a Reichert Thermopan melting point microscope and are uncorrected.

2.2. Synthesis of (acenaphthylene) $\text{Cr}(\text{CO})_3$ (**3**)

$\text{Cr}(\text{CO})_6$ was reacted to give $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ according to a literature method [16]. A mixture of 3.74 g (20 mmol) of $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ and 2.28 g (15 mmol) of acenaphthylene was heated under reflux in 150 mL of THF for 5 h. After being cooled, the solution was filtered through a celite filter and the residue was washed with CH_2Cl_2 (2×5 mL). The combined filtrates were concentrated in vacuum to a viscous purple residue. The crude product was transferred to a 5×35 cm silica gel column and chromatographed with

hexane until all of the excess yellow acenaphthylene had been eluted. The product was recrystallized from CH_2Cl_2 /hexane mixtures to give the desired product as purple crystals. Yield 3.0 g, (71%); m.p. 132–133 °C. Anal. Calc. for $\text{C}_{15}\text{H}_8\text{O}_3\text{Cr}$: C, 62.51; H, 2.80; Cr, 18.04. Found: C, 62.72; H, 2.84; Cr, 17.93. IR (KBr, cm^{-1}): ν (CO) 1976 (s), 1850 (s). ^1H NMR (500 MHz, resonances in ppm, numbering from Fig. 1): δ 7.54–7.57 (t, 1H, 12-H); 7.63 (dd, 2H, $J = 7.5$ Hz, 11,13-H); 5.32–5.36 (t, 1H, $J = 7.2$ Hz, 6-H); 6.10–6.14 (m, 2H, $J = 6.5$ Hz, 5,7-H); 7.16 (d, 1H, $J = 5.1$ Hz, 14-H); 7.20 (d, 1H, $J = 5.2$ Hz, 15-H). ^{13}C NMR (CDCl_3 , 125 MHz, resonances in ppm, numbering as in Fig. 1): δ 88.7, 90.1 and 92.7 C5, C6 and C7; 101.3,

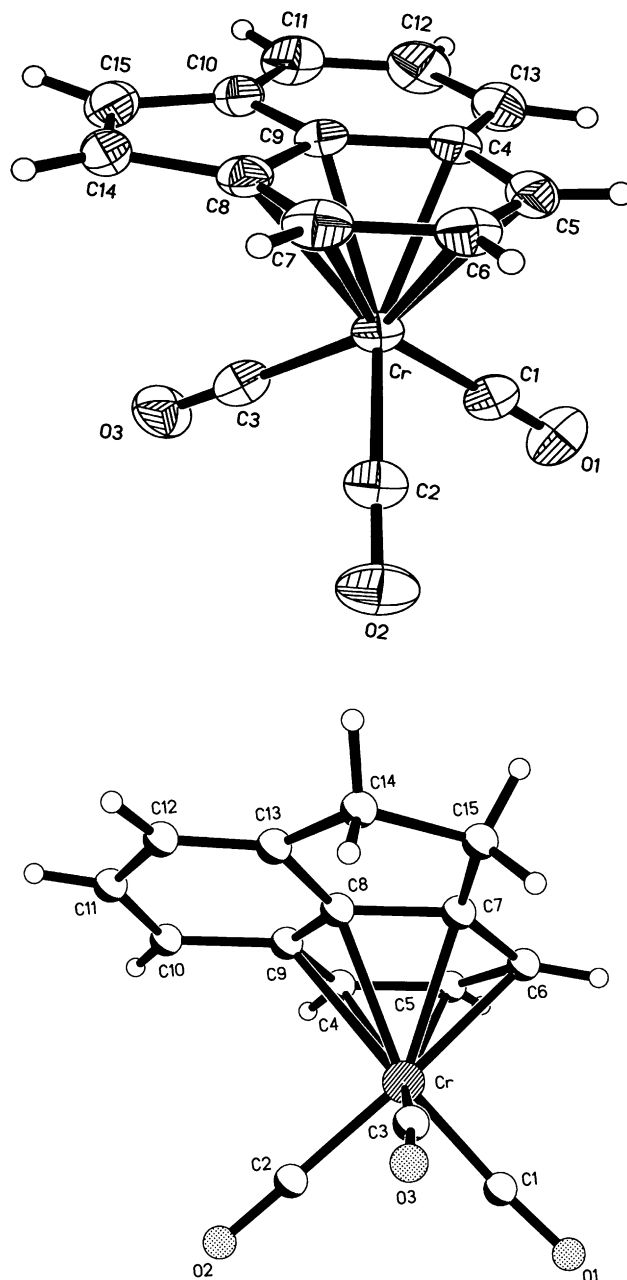


Fig. 1. ORTEP diagram of **3** (top) and **4** (bottom) with thermal ellipsoids at the 30% probability level.

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